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THE UNIVERSITY OF ALBERTA

RATES OF MIGRATION OF ALKALI AND STRONTIUM IONS IN A HEATED QUARTZ MONZONITE

by

© SUSANNA KESMARKY

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "Rates of migration of alkali and strontium ions in a heated quartz monzonite", submitted by Susanna Kesmarky, in partial fulfilment of the requirements for the degree of Master of Science.

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ABSTRACT

Samples of the Prosperous Lake Granite were heated in air at 890°C for periods of time varying from 2.5 to 1079 hours, resulting in the migration of Na, K, Rb, and Sr^{87r} ions between the mineral constituents of the rock. Electron microprobe analysis demonstrated the occurrence of Na and K exchange between albite and the K-minerals (biotite, muscovite, and microcline). Biotite lost approximately 30% of its original Rb and Sr^{87r}, and muscovite lost 15% of its Sr^{87r} and gained an additional 10% Rb by 1079 hours of heating. No other elements migrated between minerals as a result of heating.

Using a diffusion model, coefficients for migration or diffusion for the above ions of 10^{-15} to 10^{-12} cm^2/sec were calculated. Volume diffusion of K into albite appeared to be the limiting factor in Na-K exchange in the rock. The driving force for such significant alkali exchange to occur was undoubtedly a result of changes in equilibria at the high temperatures employed.

The micas were dehydrated, with biotite undergoing considerable decomposition on a micrometre scale (but with no overall change in composition except for alkali ions) during the course of the experiment. Ionic migrations appeared to occur by non-volume diffusion in the micas. Nevertheless, rapid loss of radiogenic Sr from biotite and muscovite, with no comparable movement of other divalent cations was observed. The situation was therefore analogous to the migration of radiogenic Sr during metamorphism, illustrating the importance of thermodynamic as well as kinetic factors under both experimental and natural geologic conditions.

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INTRODUCTION

The implements of the scientific method include observation, formation and testing of hypotheses, and experimentation. Utilizing mainly the first two of these investigative aids, the early geologists' task of determining events in earth history was akin to the deciphering of hieroglyphics. With the experiment already complete, it was necessary to work backwards to deduce the conditions from the results. However, the techniques of both observation and experimentation have become increasingly sophisticated, and it is now possible to simulate some geologic processes in the laboratory.

In the study of geologic events in time, the development of isotope geochronology has proven invaluable. There are three main radioactive decay schemes presently in common use for the dating of rocks and minerals: those of the potassium-argon, rubidium-strontium, and uranium/thorium-lead nuclide pairs. In order for one of these radiometric "clocks" to yield meaningful ages of crystallization of geologic units, it must be assumed that the rock or mineral being dated has been a closed system, i.e. closed to loss or gain of both parent and daughter nuclides since the time of its formation. However, discordances are often present between the ages yielded by the different radiometric decay systems. Also different minerals from a given rock may give discordant radiometric ages using only a single decay system. Thus very few geologic systems can be considered strictly "closed" from the point of view of radiometric dating.

Analytical dates obtained by these methods may sometimes be inferred to relate to major geologic events, e.g. metamorphism or in-

trusion (Moorbath, 1967), if the minerals or rocks have recrystallized or equilibrated with respect to parent and daughter nuclides on a hand specimen or regional scale during the event. Re-equilibration occurs due to thermodynamic instability, and to the increased mobilities of ionic species in minerals resulting from the increased temperature and/or pressure. In particular, daughter nuclides of radioactive decay would be expected to occupy thermodynamically and geochemical unstable niches, and likely would relocate to more favorable sites. Thus, dates obtained depend on geochemical migration, or diffusion, which in turn depends on temperature and other parameters. Significant diffusion may occur well below crystallization temperatures, at temperatures which may be maintained for many millions of years after crystallization. Later, small thermal events may also result in diffusion of some species, yet show no evidence on petrographic examination. Therefore, in areas of complex geologic history, with discordant ages, the dates themselves may have almost no time significance (Moorbath, 1967).

When can one assume equilibrium, or that rock systems have been closed? What are the rates and temperature dependence of diffusive processes in rocks? The geochronologist needs answers to these questions to unravel geologic history. But such questions lie within the realms of the physical chemist! Nevertheless, the kinetics of diffusive processes constitutes a subject which is assuming great importance in all branches of geology, including geochronology. The upsurge of interest in this area of research is evidenced by the publication of Geochemical Transport and Kinetics (1974) by the Carnegie Institute of Washington. In particular, the paper by B.J. Giletti pertains to diffusion as related to geochronology and summarizes research in the area

up to 1974. The following discussion is concerned mainly with work relevant to diffusion involving the Rb/Sr method of dating.

A common pattern could often be discerned in discordant Rb/Sr mineral ages, leading to the development of the isochron plot by Nicolaysen (1961, in Faure and Powell, 1972). Where co-existent minerals had re-equilibrated with respect to strontium isotopes during a metamorphic event, the mineral isochron could be used to date the event, since the initial strontium isotopic composition would not have to be assumed. Subsequent interpretations of discordant ages obtained by the Rb/Sr method have presupposed redistribution of radiogenic Sr during metamorphism, analogous to loss of radiogenic argon when K/Ar dating is used.

Various researchers have studied the diffusion of radiogenic nuclides in geologic field settings affected by a thermal event, e.g. contact metamorphism. Hart et al. (1968) discussed the discordant mineral age relations in the vicinity of a granitic intrusive, the Eldora stock. Rb/Sr and K/Ar ages were determined in the Precambrian basement rocks at varying distances away from the contact. All mineral ages were found to increase (to variable extents) with distance away from the contact, and a hierarchy of stability of the mineral ages to the thermal metamorphism was also established. Heat flow models were used to estimate temperature as a function of distance from the contact. The age variations were then described in terms of simple diffusive loss of the daughter products, argon and strontium, assuming spherical diffusion geometry. Diffusion coefficients were calculated using the ages to determine the amount of loss of these nuclides, and were plotted according to an Arrhenius relationship, using temperatures obtained by the heat flow models. Activation energies on the order

of 15 to 30 kcal/mole (depending on the heat flow model used) for the diffusion of argon and strontium in biotite were obtained. The effect of grain size on losses of radiogenic Sr in biotite was also investigated. Fine-grained biotite yielded lower Rb/Sr ages than coarse grained biotite. The radial distribution of Rb, K, and Sr in flakes of biotite was studied. Radiogenic strontium was found to decrease, normal strontium to increase, and potassium and rubidium to remain essentially constant (decrease slightly) in concentration from the center to the rim of the grain. The above results indicated that low Rb/Sr ages were indeed due to loss of radiogenic strontium, and not to gain of rubidium, and that diffusion was controlled by particle size.

A similar study was carried out by Hanson and Gast (1967) on the effects of thermal metamorphism near the contacts of two mafic intrusives. Activation energies of 50 to 75 kcal/mole for the loss of radiogenic argon and strontium due to simple volume diffusion were obtained. A more general mathematical formulation for describing the kinetics of contact metamorphism was given by Gray (1971). The above studies have yielded variable results due to the assumptions involved and the requirement for having an accurate model of the thermal history in order to determine diffusivities.

The other main approach to investigate diffusion of geochronologically important nuclides has been to study the self-diffusion* of these nuclides in pure minerals under controlled laboratory conditions. Geologic processes are not amenable to direct observation or even repro-

---

*self-diffusion, the migration of a single atomic species, usually studied using isotopic tracers, as compared to interdiffusion, diffusion characterized by exchange of one ionic species for another (Giletti, 1974 A)

duction due to the time factor involved. In the past ten years, experimental petrology has become more refined, so that many experimental parameters besides temperature and pressure can be controlled (Hewitt and Gilbert, 1975), however, no petrologist, no matter his longevity, can hope to conduct an experiment completely true to nature. It is therefore often necessary to employ higher temperatures or catalysts in experimental petrology, and, although limitations are inherent in the procedure, to extrapolate the results to conditions actually occurring geologically.

The diffusion of argon in many minerals has been extensively studied, but investigations of diffusion affecting the Rb-Sr system have, as yet, been few. A.W. Hofmann (1974), studying the diffusion of Ca and Sr in a dry basalt melt, found that equilibration on a centimeter scale would require a few years, but on a kilometer scale would not be complete even in the lifetime of the earth, as estimated from the magnitude of the diffusion coefficients alone. Diffusion coefficients in solid silicate systems are usually several orders of magnitude lower than in silicate melts. Most experiments have utilized isotopic exchange of minerals with hydrothermal solutions, but early studies along this line often resulted in chemical reaction instead of diffusion.

The most extensive and consistent work has been carried out by Giletti and coworkers at Brown University. Giletti (1974 A) discussed various criteria of experimental design necessary for the measurement of self-diffusion coefficients of ionic species in minerals, including stability of the mineral under the conditions of the experiment, and maintenance of electrical neutrality. The research group

employed isotopic exchange of minerals (albite, microcline, biotite) with hydrothermal solutions that were in equilibrium with the minerals, except for isotopic disequilibrium of the element under study, at 2 kbar pressure, in the temperature range from 300° to 800°C. Diffusion coefficients were estimated from experimental data assuming cylindrical or spherical diffusion geometries.

Hofmann and Giletti (1970) investigated K, Rb, Na, and Sr diffusion in biotite. The potassium diffusivity was approximately three times that for rubidium, and sodium diffused faster than potassium, but diffusion constants for Na and radiogenic Sr did not appear to differ from those for K and Rb by more than one order of magnitude. Initially, high diffusion rates were observed, after which the diffusion coefficients decreased with increasing run duration, suggesting that more than one diffusion mechanism was operative. The advent of the ion microprobe has made it possible to study very small diffusion gradients and diffusion anisotropy. The ion microprobe was applied to re-investigate the K diffusion in the above biotite, with the result that K diffusivity was found to be two to four orders of magnitude greater in the a or b crystallographic directions than in the c-axis direction (Hofmann et al., 1974). Giletti (1974 A) has also referred to preliminary results from Hofmann's and Foland's theses, indicating that for Sr diffusion in biotite and orthoclase, there appeared to be no difference in the diffusivities of radiogenic and non-radiogenic Sr.

Kasper (1974) studied cation (Na, K, Rb) diffusion in the Amelia albite, calculated diffusion coefficients assuming spherical diffusion geometry, and obtained activation energies (Q) for diffusion of these ions from 25 to 50 kcal/mole ($Q_{Rb}<Q_{Na}<Q_{K}$). The K diffusion was

again investigated by Giletti (1974 B) using an ion microprobe. An activation energy of 38 kcal/mole K in the (001) crystallographic direction was obtained. The diffusion coefficient in the (010) direction was one-tenth that in the (001) direction at 800°C.

Foland (1974) discussed alkali (Na, K, Rb) diffusion in the Benson Mines orthoclase. Both cylindrical and spherical models for diffusion were utilized to calculate diffusion coefficients, which were 2.5 times higher using the cylindrical model. Activation energies from 50 to 75 kcal/mole were obtained, increasing in the order $Q_{Na}<Q_K\leq Q_{Rb}$. Diffusivities (diffusion coefficients, D) increased in the order $D_{Rb}<D_K<D_{Na}$. Foland concluded that "for alkali diffusion" (in orthoclase) "the rates decrease and the activation energies increase with increasing ionic size." The K diffusivity was much smaller than Na diffusivity (e.g. at 800°C, $D_{Na}\sim 1000\ D_K \sim 3000\ D_{Rb}$) and the difference increased with increasing temperature, suggesting different mechanisms of diffusion between Na and K or Rb. Some ion exchange (interdiffusion) experiments of orthoclase with (K, Na) Cl solutions were also attempted. The rate of approach of the fluid to Na/K equilibrium was very slow and seemed to be governed by orthoclase K diffusion. The approach to Na isotopic equilibrium was much faster than to Na or K chemical equilibrium. Therefore Na and K appeared not to be coupled, in spite of the requirement for electrical neutrality. Foland also considered the results of investigations by other laboratories on alkali diffusion in feldspars, and concluded that diffusion was much the same in molten salt and hydrothermal experiments. Discussion of alkali diffusion in feldspars can be found in Feldspar Minerals (1974, Vol. 2, Smith, ed.).

The aforenamed experiments are beginning to yield accurate data

on the diffusion of ions in pure minerals, however, in most instances, the data cannot be directly applied to geologic field situations. In a rock, interdiffusion or reaction occurs rather than self-diffusion. The movement of an ion depends on other phases for its take up and release, and thus "the apparent age stability of the dated mineral may depend on the particular mineral assemblage it is in" (Hart et al., 1968). It would be desirable to obtain data in situations that are intermediate between field observations involving many assumptions and idealizations about diffusion, and laboratory experiments on isolated minerals involving very idealized processes as compared to what occurs geologically.

With the above point in mind, Baadsgaard and van Breemen (1970) tried to induce migration of Rb and Sr in a silicate rock, the Prosperous Lake Granite, by heating. Van Breemen (1965) had carried out some previous heating experiments on the Southeast Granodiorite. The rock was heated in air for 100 hours at 800°, 860°, 900°, 985°, and 1025°C, and the minerals were then separated and analysed for Rb and Sr isotopic compositions. The samples heated at the highest temperatures had partially fused, making the mineral separations and interpretation of results difficult. However, even at the lower temperatures, there were significant changes in the Sr^{87}/Sr^{86} ratios and the Rb, Sr, K, and Na concentrations in the individual minerals, whereas the whole rock had not changed in composition. The Sr isotopic compositions changed in the direction of isotopic homogenization. Muscovite and oxidized biotite were found to lose Rb and radiogenic Sr, and to gain normal Sr, with the overall result that biotite would give too high and muscovite too low apparent ages. Albite, and to some extent apatite, appeared to gain the radiogenic Sr lost by the other phases. Potassium from the K-contain-

ing minerals (microcline, muscovite and biotite) and Na from albite were found to have exchanged to some extent with each other. Microcline and albite, in particular, had undergone considerable mixing with respect to alkali composition.

The investigation with which the present thesis is concerned, was a continuation of the research by Baadsgaard and van Breemen. It was desired to study the rates (kinetics) at which ionic relocation was occurring and the relationship of changes in the Rb and Sr composition to changes in major element chemistry of the minerals. To this purpose, further heating experiments were carried out at a single temperature for a series of different time intervals.

SAMPLE DESCRIPTION

The sample selected for this experimental study was the Prosperous Lake Granite. This rock is actually of quartz monzonitic composition, consisting almost entirely of quartz, albite (sodic oligoclase), microcline, muscovite and biotite. Chemical and modal analyses and petrographic description are given by Baadsgaard and van Breemen (1970).

EXPERIMENTAL PROCEDURES

A. Heating Procedure

From previous work carried out by Baadsgaard and van Breemen, it was decided to choose a heating temperature and heating times such that measurable compositional changes occur during reasonably short times, but where the temperature is below that where fusion would occur or where mineral separations would become too difficult. Thus, the temperature selected was 890°C, and heating experiments were carried out for varying periods of time (from 2.5 to 1079 hours) in order to follow the kinetics of atomic or isotopic relocation.

An unweathered piece of the rock was cut into approximately one inch cubes, which were intermixed in order to minimize large scale inhomogeneity in the rock. These cubes were placed in a furnace in room atmosphere around a platinum-platinum 13% rhodium thermocouple, but were kept from direct contact with the thermocouple by small pieces of the rock. The desired temperature of 890°C (9.1 millivolt reading on the thermocouple) was reached in two hours, and the time at two hours was taken to be zero time, to mark the beginning of the experiment. Once the 890° temperature was reached, it was found not to vary more than 20°C from the desired value.

Four cubes from different locations in the furnace were removed at each of the following times: 25, 50, 100, 213, 405, 802, 1079 hours, and thus were quickly cooled to room temperature. The temperature in the furnace was observed to fall momentarily while the samples were being removed, but was re-established in 15 minutes.

Short term heating was also carried out on four to five cubes of sample each time for 2.5, 5, 10, and 20 hours. In these cases, the furnace was brought to 890°C and the samples cubes inserted quickly into the hot furnace. The temperature was re-established at 890°C in 15 minutes.

Five different pieces of Prosperous Lake Granite were left unheated, but were subjected to the same sampling and analytical procedures as the heated samples. These unheated samples were to be used as a standard for comparison of the results due to heating. Several unheated samples were necessary to elucidate to what extent results would be affected by compositional heterogeneity of the sample.

B. Mineral Separation

Both heated and unheated samples were crushed and sieved. The 80-150 mesh size fraction of each sample was retained for mineral separations. For most of the heated samples, particularly that for 405 hours (approximately 60-80 mesh), a slightly coarser grain size was used.

A combination of density and magnetic properties was utilized to separate the constituent minerals. Sinking or floating in various proportions of tetrabromoethane and acetone (or methylene iodide and acetone) was alternated with use of the Frantz isodynamic separator.

Mineral separates of approximately 95% purity could be obtained in this manner.

The heated microcline and albite could not be completely separated free of contamination from each other, due to their partial alkali-homogenization. By optical inspection, the mica separates appeared to be very pure. After one set of isotopic data on the unheated muscovites yielded variable results, however, it appeared that there must still be contamination from other minerals. All the micas were therefore further purified by sliding them along a piece of paper. The fine sheets of mica remained behind, and round grains were rolled off the paper. By this method another 2 to 3% of impurity, consisting of feldspars, quartz, and apatite, could be removed. The finally purified micas were left with essentially no contaminant grains of other minerals evident on optical examination. Although some impurity still remained as inclusions between mica sheets, it was impossible to eliminate this source of contamination. Because of the gross underestimation of this type of impurity by optical inspection, and later variability of results on the unheated micas, the final purified mica separates were estimated to be 98-99% "pure". Possibly acid washing would have removed some feldspar and apatite impurity, but this procedure was not carried out. There was not enough mineral separate available to purify the longest heated mica samples as much as desired.

C. Heating of Mineral Separates

Approximately one gram samples of the purified unheated biotite, muscovite, and microcline were subjected to heating in porcelain crucibles at 900°C in a furnace. The weight loss after 2.5 hours was found to be 4.30% for the muscovite, 0.07% for the microcline, and 1.87% for the

biotite. No additional significant weight changes were observed on further heating to a total of 23 hours at 900°C, and then at 1150°C for another hour. If it is assumed that all the ferrous iron in biotite is oxidised by atmospheric oxygen during heating, the 1.87% weight loss corresponds to a loss of 4.08% water. This assumption is justified by data on H_2O and FeO-Fe_2O_3 contents in the heated and unheated micas (Baadsgaard and van Breemen, 1970).

RESULTS AND DISCUSSION

A. Rb and Sr Isotopic Analytical Data

1. Unheated minerals

The five specimens of unheated rock and the minerals separated from them have been designated A to E. Rubidium and strontium analyses on the minerals are presented, each analysis referring to data from one, or the average of two mass spectrometric runs. It is believed that each run had an analytical precision of approximately 0.5%, as indicated in the appendix, and confirmed by the reproducibility of results when two mass spectrometric runs were performed on the same sample. When two results for the same sample are reported, it is implied that two separate decompositions for different aliquots of the same mineral separate were carried out. It should be noted that different decomposition procedures were employed for Rb and Sr analyses, thus, different portions of the mineral separate were sampled. The average results on the unheated minerals A to E are tabulated. Reproducibilities are expressed in terms of standard deviations quoted at the 1σ level.

Isotopic data for unheated microclines, muscovites, and biotites are presented in Tables I, II, and III respectively. The unheated albites were not completely purified nor analysed mass spectrometrically. The following notation is used to present data in the tables:

Sr^{N}	- concentration of normal Sr in p.p.m.
Sr^{87r}	- concentration of radiogenic Sr in p.p.m.
Rb	- concentration of Rb in p.p.m.
*	- single filament Rb analysis.
**	- triple filament Rb analysis.

TABLE I

Rb and Sr in Unheated Microclines

Microcline Sample	Sr^{N} (p.p.m.)	Sr^{87r} (p.p.m.)	Rb^{*} (p.p.m.)
A	158.8	6.33	621
B	164.9	6.17	610
C	160.7	6.29	616
D	162.5	6.29	626
E	167.9	6.23	618
Average Unheated	163 ± 4	6.26 ± 0.07	618 ± 6

* - single filament Rb analysis

TABLE II

Rb and Sr in Unheated Muscovites

Muscovite Sample	Sr^{N} (p.p.m.)	Sr^{87r} (p.p.m.)	Rb (p.p.m.)
A'	?	?	604*
B'	9.13	5.94	584*
C'	8.32	6.17	601*
D'	8.70	5.99	597*
E'	8.41	6.13	586*
Average Unheated	8.6 ± 0.4	6.06 ± 0.11	594* ± 10
A"	6.98	6.30	605**
B"	8.18	6.14	586**
C"	8.09	6.20	598**
D"	8.38	6.21	591**
E"	7.45	6.13	588**
Average Unheated"	7.8 ± 0.7	6.20 ± 0.08	594** ± 8

? - sample lost

' - initially purified samples, see text

" - further purified samples, see text

* - single filament Rb analysis

** - triple filament Rb analysis

TABLE III

Rb and Sr in Unheated Biotites

Biotite Sample	Sr^N (p.p.m.)		Sr^{87r} (p.p.m.)		Rb (p.p.m.)	
A	4.73 4.72	4.73	14.41 14.28	14.35	1436* 1455**	1446
B	4.87 4.84	4.85	14.05 13.90	13.98	1433* 1411**	1422
C	4.77 4.66	4.72	13.77 13.74	13.75	1407* 1381**	1394
D	4.75 4.54	4.65	13.97 13.51	13.75	1439* 1399**	1418
E	5.78 5.47 5.70	5.65	14.03 13.46 13.90	13.90	1400* 1415**	1408
Average Unheated		4.9 ± 0.5		13.95 ± 0.25		1418 ± 25

* - single filament Rb analysis

** - triple filament Rb analysis

The results in Table I are essentially identical with those reported by Baadsgaard and van Breemen (1970) for unheated microcline. The sampling variability can be seen to be several percent for normal Sr and approximately 1% for radiogenic Sr and for Rb.

For the muscovites, two sets of analyses were carried out, one on the initially purified minerals (samples A' to E') and another after further purification (samples A" to E") by rolling out impurities. The average value for the unheated muscovite demonstrates a large uncertainty in analysis due to sampling, 5 to 10% in normal Sr and approximately 2% in Rb and radiogenic Sr. The further purified muscovites contain an average of approximately 1 p.p.m. less normal Sr than the initial samples. It is estimated that less than one percent of a mixed feldspar impurity can account for the discrepancy. A variable degree of contamination plus actual sample variation must be responsible for the large range in normal Sr values obtained.

The unheated biotites again show an uncertainty of about 10% in normal Sr and 2% in Rb and radiogenic Sr due to sampling. The large uncertainty in Sr^N is believed to incorporate variable degrees of contamination, and the variation in Rb and Sr^{87r} to reflect mainly sample inhomogeneity. The present data on unheated muscovite and biotite do not vary greatly from those reported by Baadsgaard and van Breemen (1970), except for Sr^N in biotite. The difference is attributable to the much greater purity of the biotite samples used in the present study, particularly due to the finer grain size of the mineral separates.

The average values for unheated muscovites and biotites from Tables II and III were converted to correct for weight loss on heating (4.3% for muscovite, 1.87% for biotite (Experimental Procedures)) in order to allow comparison with the heated samples. The muscovite values

were divided by 0.957 and biotite values by 0.981 to yield results which are included with data on the heated minerals under the notation of "0 hour sample". The errors due to sample variability and contamination as determined on the unheated samples are assumed to apply to each of the heated samples also.

2. Heated Muscovites and Biotites

Results on the heated muscovites and biotites are detailed in Tables IV and V respectively. Samples are referred to by the length of the heating time. The data on the heated muscovites indicate no significant changes in Rb and Sr^{87r} concentrations until the 405 hour sample. As shown in Table IV, average values for samples heated for 2.5 through 100 hours are almost identical with results for the unheated samples. For heating times greater than 100 hours, there is a decrease in radiogenic Sr, and an increase in Rb contents of the muscovites. Because of the large sample variation, it is difficult to discern any concentration changes in normal Sr; however, Sr^{N} has probably decreased slightly with heating, especially since the longer heated muscovites were apparently more contaminated with impurities containing Sr^{N}. The variations in normal Sr deem it futile to consider $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ ratios. Instead, only concentrations have been tabulated and will be considered in the discussion.

The heated biotites again do not display noticeable concentration changes until approximately 100 hours of heating, when both Rb and Sr^{87r} begin to decrease. Normal Sr is slightly higher in all the heated samples than in the average of the unheated samples. The difference is most likely due to increased contamination of the heated samples because of

their larger grain size. The coarsest grained sample, 405 hour biotite, has the highest concentration of Sr^N, warranting the above supposition. It is thus not possible to make any statements about changes in Sr^N in the biotites - Sr^N may stay the same with heating, or even decrease, the decrease being masked by an increase from increasing amounts of impurities.

By 1079 hours of heating time, muscovite has lost approximately one-sixth of its radiogenic Sr, and gained an additional one-sixth Rb. Biotite at 1079 hours, has lost approximately one-third of both its radiogenic Sr and Rb. The results obtained indicate that a steady state or equilibrium has not been reached by 1079 hours, since the values are still changing.

TABLE IV

Rb and Sr in Heated Muscovites

Muscovite Sample# (Heating Time - Hours)	Sr^N(p.p.m.)		Sr^{87r}(p.p.m.)		Rb(p.p.m.)	
0'	9.0 ±0.5		6.33±0.12		621* ±11	
0"	8.15±0.8		6.48±0.09		621**±10	
2.5	7.00		6.14		618**	
5	9.52		6.38		612**	
10	7.72		6.48		621**	
15	8.33	8.1±0.8	6.32	6.35±.12	615**	618±10
20	8.82		6.26		607**	
25	7.73		6.52		630**	
50	8.03		6.33		618**	
100	7.50		6.37		626**	
213	7.19 7.32	7.25	6.32 6.27	6.30	636**	
405	6.22 6.17	6.20	6.12 5.99	6.06	655**	
802	8.03 7.94	7.99	5.59 5.56	5.58	670**	
1079	6.14 6.13	6.13	5.40 5.34	5.37	678**	

0' - unheated muscovites, initially purified samples

0" - unheated muscovites, further purified samples

- all heated samples had undergone the same separation procedures as the further purified unheated muscovites

* - single filament Rb analysis

** - triple filament Rb analysis

TABLE V

Rb and Sr in Heated Biotites

Biotite Sample (Heating Time - Hours)	Sr^{N} (p.p.m.)	Sr^{87r} (p.p.m.)	Rb (p.p.m.)
0	5.0 ± 0.5	14.2 ± 0.25	1445 ± 25*
2.5	5.97	15.32	1604, 1542 } 1573**
5	6.40	15.30	1498**
10	6.60	14.67	1470**
15	6.76	14.47	1458**
20	6.66	14.82	1455**
25	5.78, 6.15 } 5.97	12.78, 14.17 } 13.48	1421**
50	6.71	14.55	1410**
100	6.69, 7.14 } 6.91	13.90, 13.98 } 13.94	1354**
213	7.10, 7.25 } 7.17	14.08, 14.01 } 14.04	1346**
405	7.76, 7.78 } 7.77	12.74, 12.72 } 12.73	1165**
802	6.30, 6.24 } 6.27	10.08, 10.14 } 10.11	943**
1079	6.89, 6.69 } 6.79	10.05, 9.93 } 9.99	968**

** - triple filament Rb analysis

* - average of single and triple filament Rb analysis

3. Discussion of Changes in Rb and Sr^{87r} in Muscovite and Biotite with Heating

The results in the previous section indicate that atomic migration or relocation has occured between the minerals of the Prosperous Lake Granite. In order to quantify the changes occurring, diffusion processes may be considered. Simple diffusion models can be used to solve the diffusion equation as described by Fick to obtain expressions relating concentration to distance and time, usually in terms of error functions. Jost (1960) has given the following approximation (equation [1]) for diffusion out of or into a cylinder, sphere, or infinite thin plate, assuming constant diffusion coefficient and time to be sufficiently large.

$$[1] \quad \frac{\bar{c} - c_f}{c_i - c_f} \sim \frac{m}{k^2} e^{-tk^2 D/r^2}$$

where t = time
D = diffusion coefficient
r = radius of cylinder or sphere, or thickness of plate
$\bar{c}$ = average concentration at time t in cylinder, sphere, or plate
c_i = initial concentration at time zero
c_f = final (equilibrium) concentration at infinite time
k = π (plate or sphere), 2.405 (cylinder)
m = 6 (sphere), 4 (cylinder), 8 (plate)

However, the above type of equation cannot be applied to data in the present experiment, because no final or equilibrium values for concentrations could be obtained, and times were probably not sufficiently long for the above approximation to hold.

Equation [2] was also provided by Jost for diffusion out of or into a finite plate (thickness r) with the variables having the same meaning

as defined previously.

$$[2] \quad \frac{\bar{c}}{c_i} = 1 - \frac{2\sqrt{Dt}}{\sqrt{\pi}\, r/2} = 1 - \frac{4\sqrt{D}}{r\sqrt{\pi}}\sqrt{t}$$

Presumably similar relationships exist for other diffusion models with only the constants varying with the model. For example, Crank (1975) outlined another approximation (equation [3]) for a circular disk source (radius r) diffusing into an infinite plane, for small times and assuming the concentration at the surface of the disk to remain constant.

$$[3] \quad \frac{\bar{c}}{c_i} = 1 - \sqrt{\frac{2Dt}{\pi r^2}} = 1 - \frac{\sqrt{2}\sqrt{D}}{r\sqrt{\pi}}\sqrt{t}$$

In general, for diffusion into a semi-infinite medium, with zero initial concentration, and the surface of which is maintained constant, the amount of diffusing substance entering the medium through unit surface of its area varies as the square root of time. This property generally holds in semi-infinite media (for point, line, spherical, cylindrical sources) provided the initial concentration is uniform and the surface concentration remains constant (Crank, 1975). Lin and Yund (1972) also have stated that data fitting the above "square root of time" law provide good evidence for the occurrence of mainly one type of diffusion process, e.g. volume diffusion, with little contribution from other transport processes, e.g. grain boundary diffusion or recrystallization.

The "square root of time" relationship has been applied to data from the present experiment, in spite of the assumptions involved. The initial concentrations were uniform and biotite and muscovite can perhaps be considered as sources in semi-infinite media, since these minerals

constitute only 2.2% and 7.7% of the rock, respectively (Baadsgaard and van Breemen, 1970). Values for square root of time versus time are presented in Table VI, and were used in conjunction with data from Tables IV and V to arrive at Figures 1 and 2.

TABLE VI

Square Root of Time for Heating Times Employed in Experiment

Time t (hours)	0	2.5	5	10	15	20	25	50	100	213	405	802	1079
$\sqrt{\text{time}}$ (hours$^{1/2}$)	0	1.58	2.24	3.16	3.87	4.47	5.00	7.07	10.00	14.59	20.12	28.32	32.85

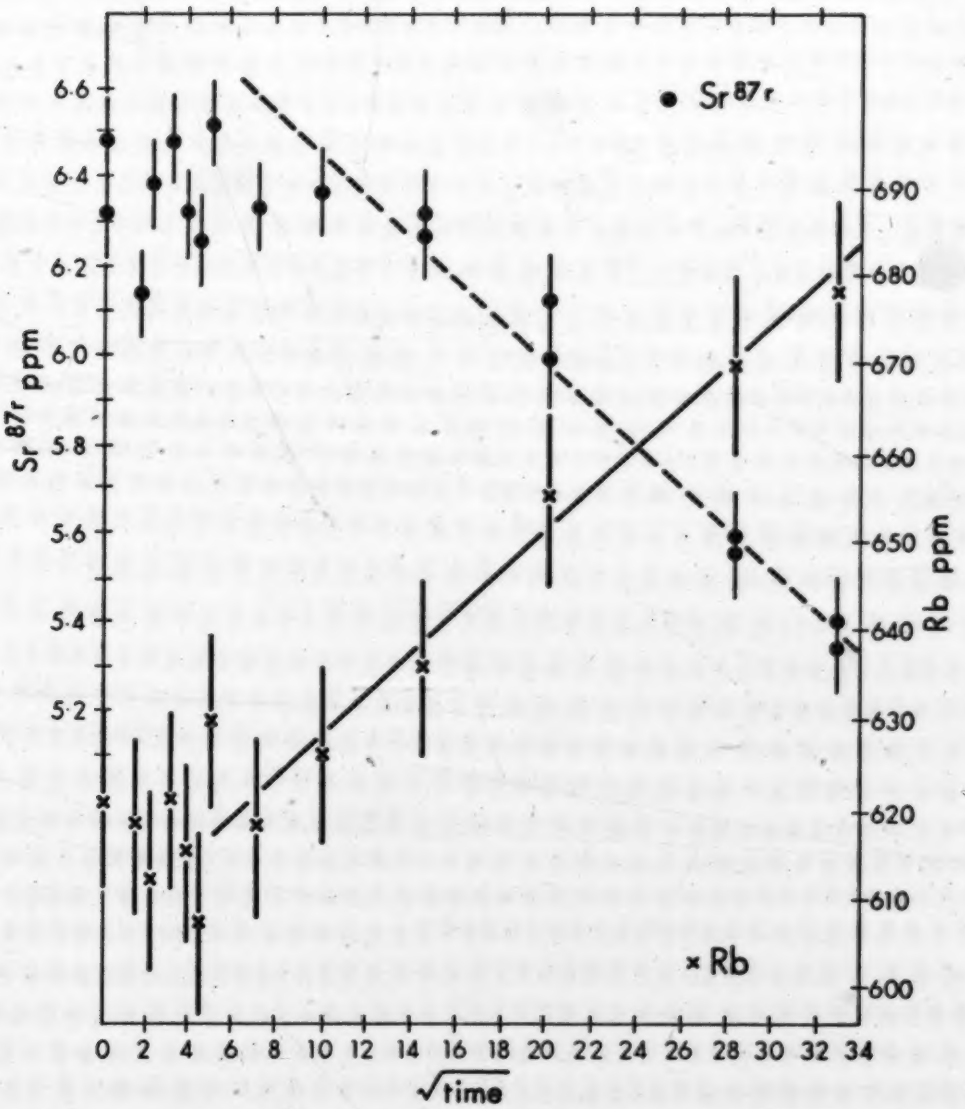

Fig. 1. Muscovites - Rb & Sr^{87r} versus $\sqrt{time}$

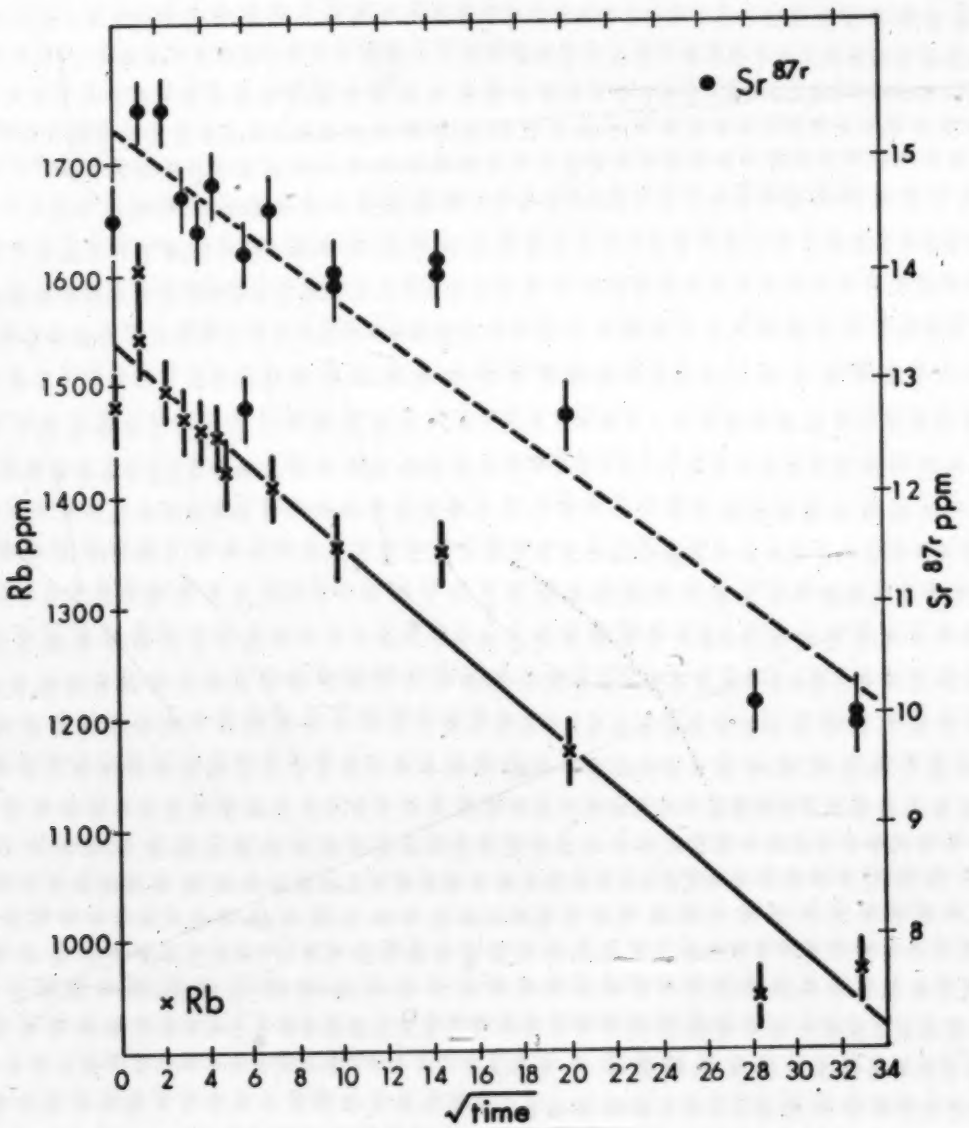

Fig. 2. Biotites - Rb & Sr^{87r} versus $\sqrt{time}$

In Figure 1, concentrations of Rb and radiogenic Sr in muscovite have been plotted against square root of time. Error bars for all samples are derived from the sampling variability in the unheated muscovites (approximately 2% for both Rb and Sr^{87r}). Initially, both curves are flat with almost zero slope but very poor correlation coefficient as calculated by least squares fitting. The zero time concentration intercept is 6.36 p.p.m. for Sr^{87r} and 617 p.p.m. for Rb. From 100 hours onwards, both curves appear linear with a slope of -0.048 p.p.m./$hour^{1/2}$ (correlation coefficient = 0.987) for Sr^{87r}, and a slope of 2.31 p.p.m./$hour^{1/2}$ (correlation coefficient = 0.993) for Rb. The initial time lag before any concentration changes have occurred could be due to the unsuitability of the model used, or to a slow process limiting migration initially, e.g. grain boundary diffusion, or loss of water from the muscovite lattice. For a graph of concentration versus square root of time, the slope equals $\frac{4\sqrt{D}}{r\sqrt{\pi}}\ c_i$ where r is the plate thickness and c_i is the initial concentration in the mineral, using equation [2]. When this equation is applied to the linear portions of the curves in Figure 1, assuming r to equal the average grain size dimension (80-120 mesh = 0.0125 cm), coefficients of diffusion of approximately 10^{-13} cm^2/sec for Rb into muscovite, and $5x10^{-13}$ cm^2/sec for Sr^{87r} out of muscovite can be calculated. Whether these numbers have true significance with respect to volume diffusion of Rb and Sr^{87r} in muscovite is unknown, since the migration rate may be related to the uptake or release of Rb or Sr^{87r} by other phases or to the rate of breakdown of muscovite.

In Figure 2, concentrations of Rb and Sr^{87r} in biotite from Table V have been plotted against the square root of time. Both plots are essentially linear from zero time, and yield a slope of -18.5 p.p.m./

hour$^{1/2}$ (correlation coefficient = 0.969) and initial concentration intercept of 1541 p.p.m. for Rb, and a slope of -0.153 p.p.m./hour$^{1/2}$ (correlation coefficient = 0.934), initial concentration intercept of 15.23 p.p.m. for Sr^{87r}, using least squares fitting. Diffusion coefficients of approximately 10^{-12} cm^2/sec for Rb and Sr^{87r} out of biotite can be calculated from the slopes using equation [2] assuming r = 0.0125 cm. The values are comparable to data of Hofmann and Giletti (1970) for the diffusion of K and Rb in biotite at 200 bars, extrapolated to 890°C, which fall in the range of 10^{-14} to 10^{-13} cm^2/sec.

In a later section of this thesis (microprobe results, biotites), the potassium concentrations of biotite were found to be extremely variable. Since Rb substitutes for K in the biotite lattice, and Sr^{87r} substitutes for Rb, it could be expected that the Rb and Sr^{87r} concentrations in biotite would also vary greatly, in addition to any variance produced by sample contamination. It is assumed that the 20 to 25 grains of biotite in each microprobe analysis result in a representative K concentration for the whole sample. Rb and Sr^{87r} concentrations from Table V for samples that were analysed using the microprobe have been corrected to a standard K concentration to eliminate the bulk of sample variability by multiplying by [K]/[Kav], where [K] is the total alkali concentration in each individual sample, and [Kav] is the average total alkali in samples 0 through 1079 hours. The results are tabulated in Table VII and the corrected Rb and Sr^{87r} concentrations plotted versus square root of time in Figure 3.

TABLE VII

Rb and Sr^{87r} in Biotite Corrected for Total K Concentration

Biotite Sample (Heating Time (hours))	[K]#	Rb&(p.p.m.)	Sr^{87r} &(p.p.m.)
0	1.57	1546	15.2
2.5	1.78	1455, 1514 } 1485	14.46
100	1.66	1338	14.07, 14.15 } 14.11
213	1.77	1278	13.36, 13.30 } 13.33
405	1.68	1165	12.73, 12.72 } 12.73
802	1.62	978	10.45, 10.51 } 10.48
1079	[Kav] = 1.70 / 1.68	957	9.93, 9.81 } 9.87

- atoms of K per 23.5 oxygens from microprobe data on biotites, Table XI

& - corrected Rb and Sr^{87r} concentrations = values from Table V x 1.68/[K]

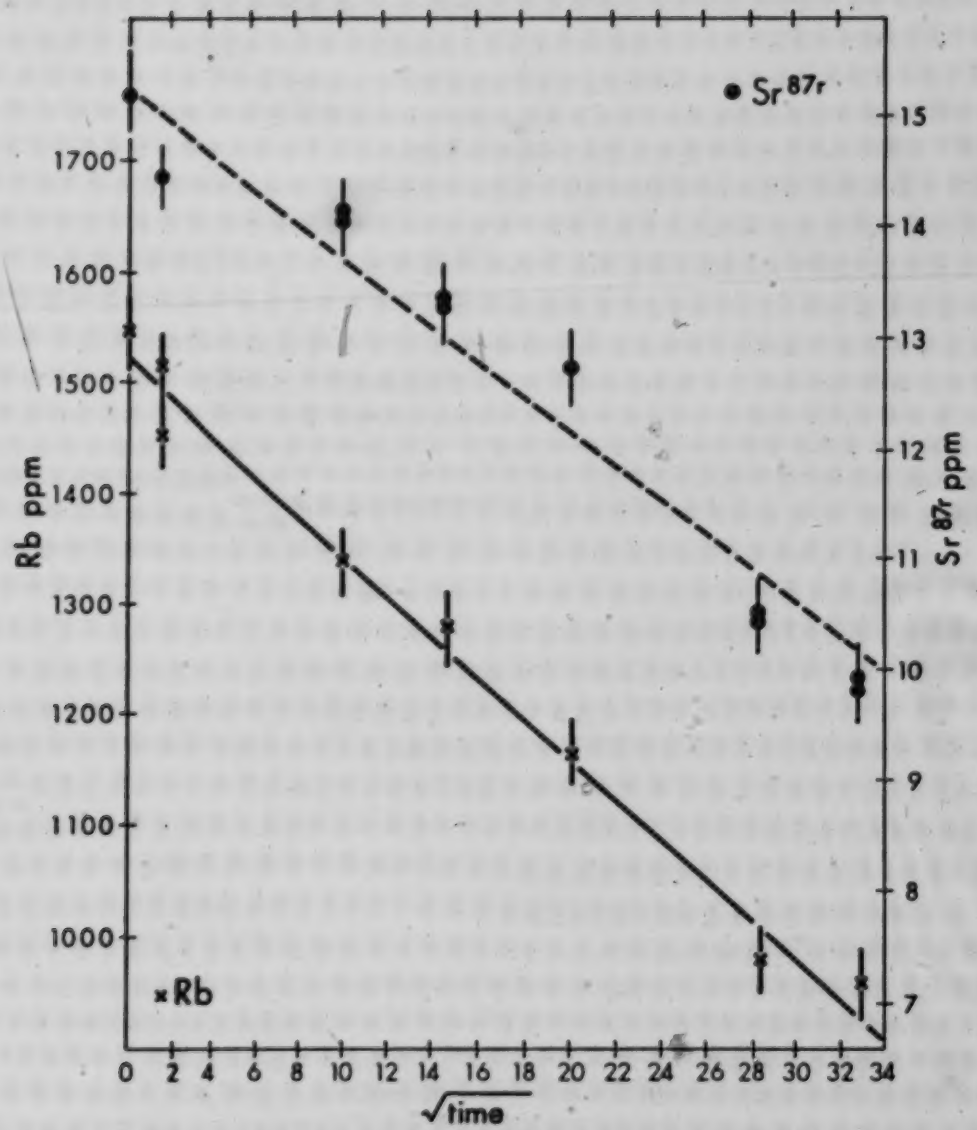

Fig. 3. Biotites - Rb & Sr^{87r} versus $\sqrt{time}$
(corrected for total K)

The lines in Figure 3 appear more linear than those in Figure 2, and yield a slope of -18.0 p.p.m./hour$^{1/2}$ (correlation coefficient = 0.994), concentration intercept of 1525 p.p.m. for Rb, and a slope of -0.156 p.p.m./hour$^{1/2}$ (correlation coefficient = 0.976), concentration intercept of 15.28 p.p.m. for Sr^{87r}. Diffusion coefficients calculated from these slopes are essentially the same as described above.

Heated albites and microclines were not analysed for Rb and Sr compositions. It was estimated from previous data by Baadsgaard and van Breemen (1970), that significant concentration changes would not be discernable or would be camouflaged because of difficulty of separating microcline and albite from each other with increased heating times.

B. Microprobe Results

1. Quantitative Energy Dispersive Analysis

Total elemental analyses are presented in terms of the number of atoms or cations for a specified number of oxygens, since most reasonably ion exchange is studied on a mole for mole or atom for atom basis. Results in terms of weight percent oxides are included in the appendix. In general, analyses (on two to four grains) in thin sections are not listed. Results on the thin sections were more variable because of the uneven surface polish, and were less representative of the sample because of the few numbers of grains analysed. Most analyses refer to beam scanning on approximately 20 to 25 grains of the grain mounts, unless otherwise indicated.

The results of albite and microcline analyses on the basis of 32 oxygens are shown in Tables VIII and IX. The sum of Na and K (total alkali), and % K/(Na+K) or % Na/(Na+K) are also given for each sample. The average of unheated albites B and E yields (Na+K+Ca)=4.06, (Al+Si)= 15.98 per 32 oxygens, and 0.33 Ca/4.06 (Na+K+Ca), making the mineral approximately 8% anorthite, i.e. an albite. The average of unheated microclines A and E yields (Al+Si)=16.94 and (Na+K+V+Ba+Zr)=3.75 per 32 oxygens. Muscovite analyses with respect to 22 oxygens and biotite analyses with respect to 23.5 oxygens can be found in Tables X and XI. A structural formula calculated for unheated muscovite B gives (Si+Al)=8.00, (Al+Mg+Fe+Ti)=3.97, and (Na+K)=1.86 per 22 oxygens. Similarly the average of unheated biotite B and 2.5 hour biotite results in (Si+Al)=8.00, (Al+Mg+Ti+Fe+Mn+Ni+Zn)=5.71, (Na+K)=1.67 per 23.5 oxygens. Mineral analyses compare favorably with those presented in Deer, Howie, and Zussman (Vol. 3, 1962 and Vol. 4, 1963).

TABLE VIII

Albites - Number of Ions Per 32 Oxygens

Albite Sample (Heating Time (hours))	Na	Al	Si	K	Ca	Na+K	$\frac{Na}{Na+K} \times 100$
0_E*	3.68	4.31	11.66	0.03	0.36	3.71	99.2
0_B	3.67	4.27	11.71	0.08	0.30	3.74	98.1
2.5	3.66	4.34	11.64	0.07	0.34	3.73	98.1
100	3.69	4.35	11.63	0.08	0.33	3.77	97.9
213	3.62	4.38	11.61	0.09	0.37	3.71	97.3
405	3.62	4.35	11.64	0.11	0.35	3.73	97.1
802	3.57	4.37	11.61	0.15	0.36	3.72	96.0
1079	3.54	4.37	11.62	0.17	0.36	3.71	95.4
1079 Ab grain#							
center of grain	3.61	4.30	11.70	0.18	0.28	3.77	95.8
rims of grain	3.25	4.31	11.70	0.41	0.31	3.66	88.8
1079 Ab grain#							
side of grain	3.54	4.40	11.60	0.09	0.39	3.64	97.3

* - thin section, average of 4 grains with hand scanning

- grain mounts, average of one grain or part of grain only with beam scanning

TABLE IX

Microclines - Number of Ions Per 32 Oxygens

Microcline Sample (Heating Time (hours))	Na	Al	Si	K	V+Ba+Zr	Ca	Na+K	$\frac{K}{Na+K} \times 100$
0_A*	0.06	4.08	11.97	3.67	0.04	----	3.73	98.4
0_E*	----	3.97	12.08	3.70	0.02	----	3.70	100.0
2.5	0.10	4.01	11.97	3.74	0.06	0.01	3.84	97.4
100	0.24	4.01	11.98	3.60	0.06	----	3.84	93.8
213	0.31	4.01	11.95	3.53	0.08	0.01	3.84	91.9
405	0.43	4.01	11.96	3.43	0.06	0.01	3.86	88.9
802	0.75	4.00	11.98	3.11	0.05	0.01	3.85	80.8
1079	0.63	4.00	11.98	3.24	0.04	0.02	3.87	83.4
1079 microcline#								
high Na grain	1.23	4.04	11.98	2.60	0.04	----	3.82	68.1
low Na grain	0.26	4.03	11.98	3.51	0.06	----	3.77	93.1

* - thin section, average of 4 grains with hand scanning

- grain mounts, average of one grain only with beam scanning

TABLE X

Muscovites - Number of Ions* Per 22 Oxygens

Muscovite Sample (Heating Time (hours))	Na	K	Mg	Fe^{III}	Ti	Al	Si	Na+K	Mg+Fe+Ti+Al	$\frac{K}{Na+K} \times 100$
0_B	0.03	1.83	0.05	0.17	0.08	5.49	6.16	1.86	5.79	98.4
2.5	0.06	1.81	0.07	0.19	0.07	5.46	6.18	1.87	5.79	96.8
100	0.18	1.71	0.06	0.18	0.09	5.47	6.16	1.89	5.80	90.5
213	0.19	1.68	0.06	0.19	0.08	5.51	6.13	1.87	5.85	89.8
405	0.19	1.69	0.04	0.18	0.08	5.53	6.13	1.88	5.83	89.9
802	0.31	1.57	0.06	0.18	0.08	5.52	6.13	1.88	5.84	83.5
1079	0.33	1.57	0.05	0.18	0.09	5.46	6.16	1.90	5.78	82.6
1079 hour muscovite#										
high Na grain	0.61	1.29	0.06	0.18	0.08	5.50	6.14	1.90	5.82	67.9
low Na grain	0.21	1.64	0.05	0.17	0.09	5.53	6.14	1.85	5.84	88.6
100 hour muscovite#										
high Na grain	0.53	1.26	0.11	0.22	0.14	5.33	6.19	1.88	5.80	67.0
low Na grain	----	1.81	0.04	0.19	0.09	5.56	6.11	1.81	5.88	100.0

- grain mounts, average of one grain only with beam scanning

* - small amounts of Ba and V neglected (Ba<0.004, V<0.02 per 22 oxygens)

TABLE XI

Biotites - Number of Ions Per 23.5 Oxygens

Biotite Sample (Heating Time (hours))	Na	K	Mg	Ti	Fe^{III}	Al	Si	Mn+Ni+Zn	Na+K	$\Sigma M^{\&}$	$\frac{K}{Na+K} \times 100$
0_B*	----	1.57	1.34	0.32	3.42	3.44	5.17	0.10	1.57	8.62	100.0
2.5+	0.02	1.76	1.24	0.36	3.26	3.37	5.31	0.10	1.78	8.33	98.8
100+	0.17	1.49	1.30	0.35	3.28	3.39	5.27	0.11	1.66	8.43	89.9
213+	0.23	1.54	1.21	0.37	3.24	3.36	5.33	0.11	1.77	8.29	87.0
405+	0.47	1.21	1.33	0.35	3.27	3.40	5.28	0.11	1.68	8.46	72.0
802+	0.63	0.99	1.30	0.35	3.23	3.41	5.30	0.13	1.62	8.42	61.1
1079*	0.63	1.07	1.26	0.36	3.29	3.35	5.30	0.13	1.70	8.39	62.9
1079 hour biotite#											
high Na grain	0.81	0.98	1.23	0.39	3.18	3.36	5.32	0.15	1.79	8.31	54.7
low Na grain	0.31	1.45	1.23	0.40	3.13	3.34	5.36	0.17	1.76	8.27	82.4
100 hour biotite#											
high Na grain	0.19	1.41	1.23	0.39	3.30	3.36	5.28	0.14	1.60	8.42	88.1
low Na grain	----	1.81	1.23	0.40	3.12	3.38	5.35	0.13	1.81	8.26	100.0

- grain mounts, average of one grain only with beam scanning

+ - average of two sets of results on grain mounts, one on 20 to 25 grains with beam scanning, the other on 20 to 25 grains with static beam

* - average of two sets of results on grain mounts, each on 20 to 25 grains with beam scanning

& - ΣM = Mg+Ti+Fe+Al+Mn+Ni+Zn

The tabulated data demonstrate that no overall changes in the concentrations of any elements, except for Na and K, has occurred in any of the minerals with heating. Also the sum of (Na+K) has remained constant, therefore only cation exchange between the Na-containing mineral (albite) and K-containing minerals (microcline, biotite, and muscovite) has resulted. The analyses of individual grains of heated minerals, presented at the bottom of each table, indicate the maximum range in concentration found when searching through heated mineral grain mounts for grains very high or low in the elements of interest (Na, K). In the 1079 hour samples, grains ranging in concentration from almost unchanged (from the unheated samples) to ones that had exchanged 1/3 to 1/2 of their K (for the K minerals) or 1/8 of their Na (for albite) could be found (see also section B.3 of Results and Discussion). The averaged analyses for each heating time hopefully do give an average value for the sample, but are bound to have a large associated error since only 20 to 25 grains were analysed.

Total (Na+K) was found to be quite variable in the biotites (Table XI), although no systematic trend with heating could be discerned. The above data was used to convert Rb and Sr^{87r} concentrations to a standard K concentration in a previous section, A.3. Also % K/(Na+K) has been used to represent $(c_t/c_i)X\ 100$, where c_t is the K concentration at time t in the mineral, and c_i the initial K concentration, for the K minerals. Analogously, the ratio % Na/(Na+K) has been used for % Na remaining in albite.

With the same assumptions as in Section A.3., the above ratios have been plotted against the square root of heating time for all the minerals in Figures 4 through 8. Error bars are not included, since

they are unknown. However, for heated minerals where the maximum concentration ranges were determined, the range is indicated by dotted lines in the figures. All the graphs demonstrate a large amount of scatter in the points, believed due in main to the uncertainty of analysis and to sample variation. Least squares fitting of the data to straight lines yields the following results: slope of -0.0993 $hour^{-1/2}$ (correlation coefficient = 0.971) for Na in albite; slope of -0.534 $hour^{-1/2}$ (correlation coefficient = 0.976) for K in microcline; slope of -1.27 $hour^{-1/2}$ (correlation coefficient = 0.980) for K in biotite; and slope of -0.462 $hour^{-1/2}$ (correlation coefficient = 0.974) for K in muscovite. As before, if equation [2] is applied to the above data (assuming the dimension over which diffusion has occurred, r, to equal 0.0125 cm) the following approximate diffusion coefficients can be calculated: 2×10^{-13} cm^2/sec for K out of muscovite and microcline, 1.5×10^{-12} cm^2/sec for K out of biotite, and 10^{-15} cm^2/sec for Na out of albite. Values for the feldspars would be approximately one order of magnitude higher if a different model for diffusion, e.g. equation [3], were employed.

The calculated diffusion coefficients for diffusion of K and Sr^{87r} out of muscovite are the same within a factor of two to three. Also, for diffusion of K, Rb and Sr^{87r} out of biotite, as would be expected from the work of Hofmann and Giletti (1970), D values obtained in the present experiment are practically identical. Diffusion coefficients obtained for K in microcline are also very similar to values previously obtained by Foland (1974) in orthoclase, Lin and Yund (1972) in K-exchanged microcline, and Petrovic (in Feldspar Minerals, 1974, Vol.2, Smith, ed.) in adularia.

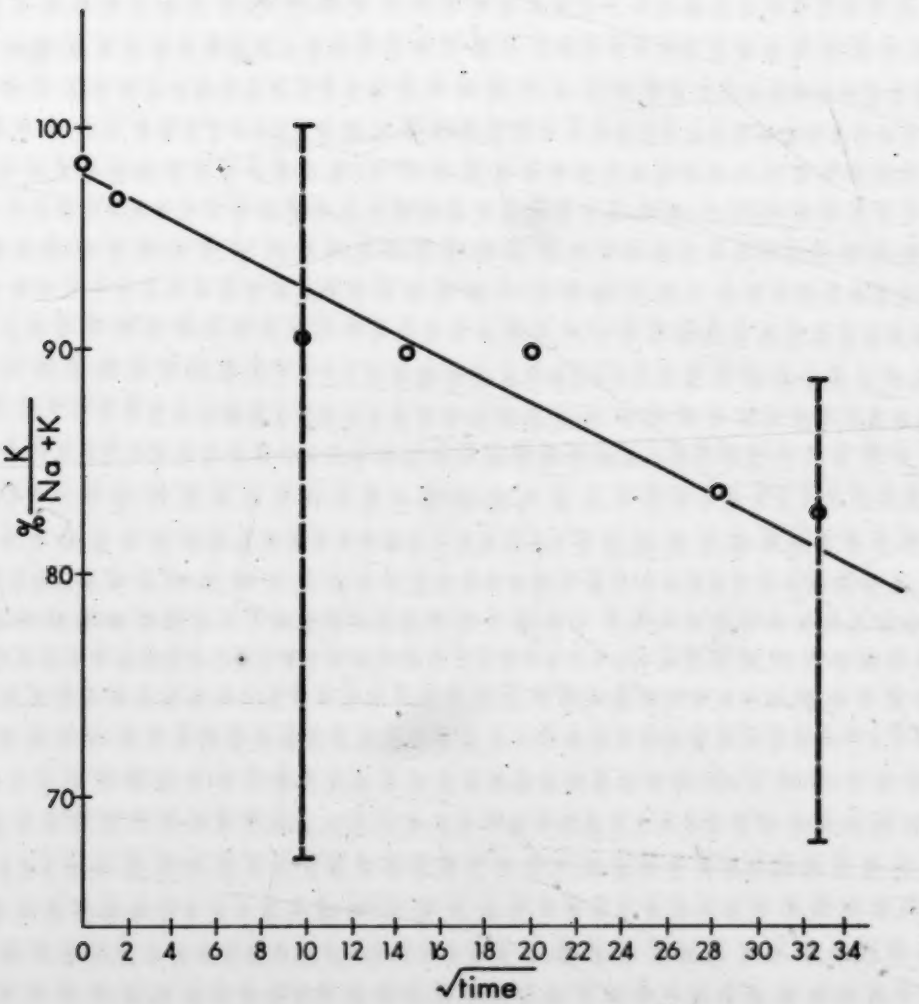

Fig. 4. Muscovites - K versus $\sqrt{\text{time}}$

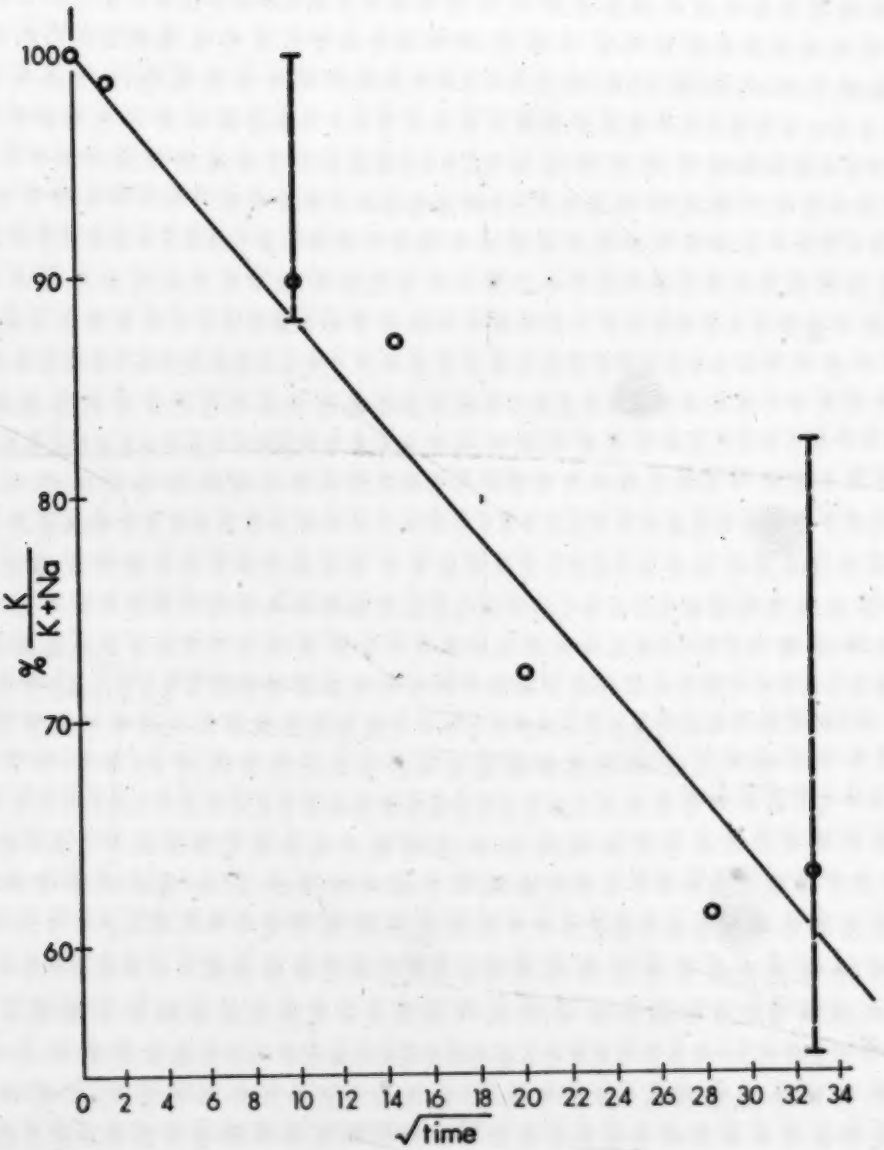

Fig. 5. Biotites - K versus $\sqrt{time}$

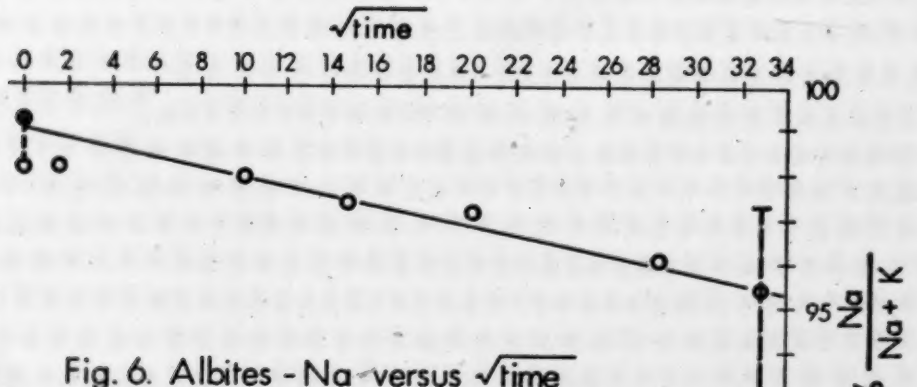

Fig. 6. Albites - Na versus √time

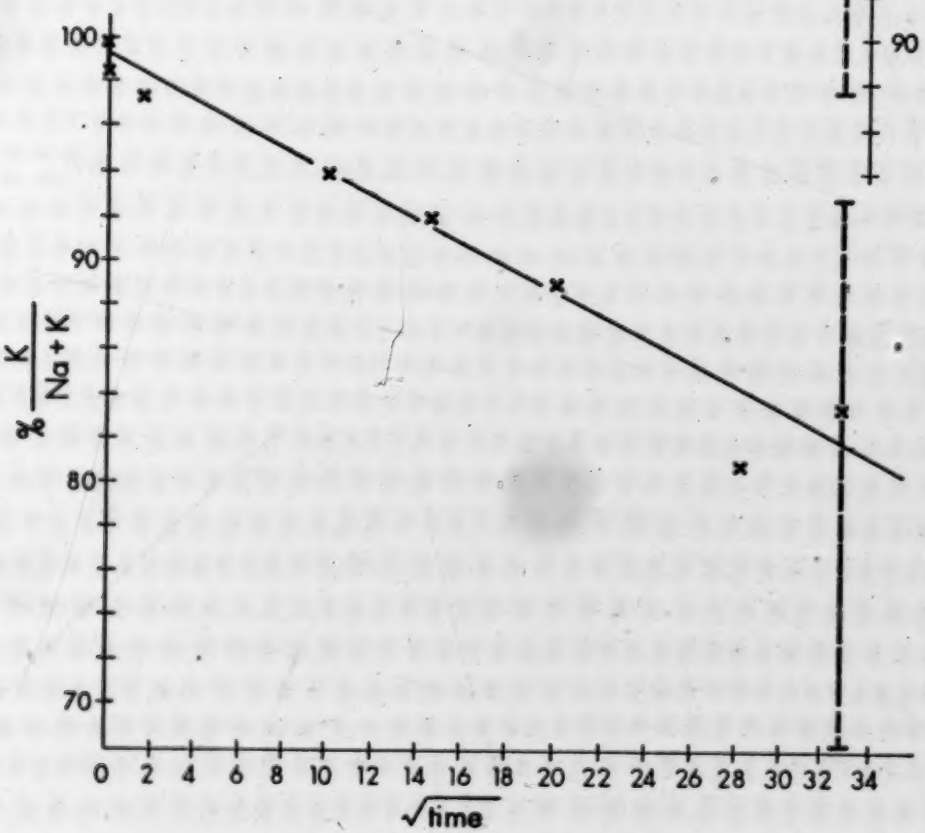

Fig. 7. Microclines - K versus √time

The coefficient calculated for albite is believed to relate to K diffusion into, rather than Na diffusion out of albite, as discussed later.

2. Discussion of Changes in Alkali Composition of Prosperous Lake Granite with Heating

The temperatures employed in this experiment lie above the microcline-albite solvus for alkali feldspars. As a result, it could be expected that alkali homogenization between microcline and albite could occur with heating. Also paragonite is appreciably soluble in muscovite at elevated temperatures (Nicol and Roy, 1965), therefore dehydrated muscovite and biotite could perhaps be expected to exchange K with Na. Although the experimental conditions employed (dry heating) are outside the stability range of muscovite and biotite, no net transport of elements other than Na and K (and Rb and Sr) appears to have occurred. The heating experiment has resulted in a process of incomplete ion exchange between minerals without equilibrium between minerals. It is common to get attainment of ion exchange equilibrium only as compared to complete equilibrium under dry or hydrothermal conditions, since the activation energy for alkali ion diffusion is lower than that for breaking framework silicate bonds (Petrovic, 1972).

In the previous sections, the highest diffusion coefficients have been obtained for K, Rb and Sr^{87r} in biotite, intermediate values for K in microcline and muscovite, and lowest values for Na in albite. However, the significance of these numbers, particularly for the major elements Na and K, is uncertain, since ion exchange (interdiffusion) has occurred rather than self-diffusion.

To consider ion exchange in the Prosperous Lake Granite, the

analogy of ion exchange between two alkali feldspars, where there is movement of cations (interdiffusion of Na and K) through a fixed anionic lattice, will be used. Petrovic (1972) and Manning (1968) have given the following expression, equation [4], for an interdiffusion coefficient, $D_{Na,\,K}$, in the above binary system, where electrical neutrality must be maintained.

$$[4] \quad D_{Na,\,K} = \frac{D^*_{Na}\, D^*_{K}}{D^*_{Na} N_{Na} + D^*_{K} N_{K}}$$

D^*_j is the composition independent tracer (self) diffusion coefficient of component j, and N_j is the fraction of cation sites occupied by component j ($N_{Na} + N_K = 1$). The expression results from the requirement for no net flux of material (to maintain electrical neutrality) in spite of the difference in mobilities of the two ions. The result is a driving force in terms of a "diffusion potential" and coupling of diffusion between Na and K.

In the case where $N_K = 1$, i.e. in the pure K mineral commencing exchange with Na, the expression reduces to $D_{Na,\,K} = D^*_{Na}$; similarly, for $N_{Na} = 1$, $D_{Na,\,K} = D^*_K$. Thus, initially, diffusion in the binary system is governed by the diffusion potential generated by the ion which is trying to get into, not by the one trying to get out of the lattice.

When the mobility of one ion is much larger than for the other, e.g. if $D^*_{Na} >> D^*_K$, equation [4] reduces to $D_{Na,\,K} = D^*_K / (1 - N_K)$, and unless $N_K = 1$, the rate of diffusion becomes determined by the mobility of the less mobile particles (Jost, 1960).

Literature on diffusion of alkalis in alkali feldspars has been reviewed extensively in Feldspar Minerals (1974, Vol. 2, Smith, ed.).

Diffusion coefficients measured under dry and hydrothermal conditions are very similar, and are little affected by variations in H_2O pressure. Petrovic (1972) has also summarized data on diffusion and interdiffusion in alkali feldspars, and stated that the self-diffusion coefficient for Na in a given feldspar is much higher than that for K in the same feldspar. For a given cation, the diffusion coefficient increases as the K/(Na+K) in the structure increases. In other words, the highest diffusion rate is for the smallest cation (Na) in the structure with the greatest volume, and the lowest rate for K in albite, as expected from simple geochemical principles. Foland (1974) found for self-diffusion in orthoclase at 800°C and 2 kbar, that the coefficient for Na was approximately three orders of magnitude greater than for K or Rb, the difference increasing with increasing temperature. Therefore, $D^*_{Na} >> D^*_K$ probably in both albite and microcline, and the interdiffusion coefficient in alkali feldspars can be estimated, as above, to be mainly determined by K diffusivity, except in the very pure microcline end-member. It should be noted that the expression for the interdiffusion coefficient is actually an approximation, since in reality the self-diffusion coefficients for an ion, e.g. Na^+, in the different alkali feldspar end-members differ, and cannot be assumed constant over the whole composition range (Petrovic, 1972).

Data from the present experiment make more sense in light of the above discussion. As indicated in a later section, the heated K minerals were relatively homogeneous, with few concentration gradients and so microprobe analyses are close to representative for whole grains. Then, the diffusion coefficients obtained on Na-K exchange for muscovite,

biotite, and microcline, in qualitative terms, probably refer to values intermediate between the self-diffusion coefficients of Na and K, or to interdiffusion coefficients. In these minerals, diffusion occurs faster in biotite, and slower and at approximately the same rate in muscovite and microcline.

Albite grains, however, showed high gradients in K concentration (section B.3,4), and only the central relatively unchanged areas (approximately 20 x 20 microns^2) were analysed using energy dispersive analysis, not yielding representative analyses of whole grains. From material balance considerations, the summation of K-diffusion out of the K-minerals, and K diffusion into albite should be identical, and result in the same interdiffusion coefficient. The values obtained in albite, however, not being representative of whole grains, but only of the almost unchanged albite central portions of grains, must refer to the diffusion of K into albite (assuming $D^*_{Na} >> D^*_K$), which is much slower than any of the other diffusion processes.

The limiting factor in alkali ion exchange in the Prosperous Lake Granite appears to be the diffusion of K into albite. This slow process determines the availability of Na to the remaining minerals. Once out of albite, Na and K interdiffuse more rapidly through the K minerals, with a resultant lack of concentration gradients in these minerals.

In general, the results of the experiment agree with previous work on interdiffusion in feldspars. Calculated diffusion coefficients are also in agreement with values obtained under dry and hydrothermal conditions in pure minerals, for solid state volume diffusion.

3. Wavelength Dispersive Analysis

Two 50-second counts per grain using wavelength dispersive analysis on the electron microprobe were carried out on five to ten random grains of the 1079 hour and unheated (and/or 2.5 hour) minerals. The three spectrometers were set at the Kα x-ray wavelengths for Si, Na, and K for biotite and muscovite, and at Ca, Na, and K wavelengths for albite and microcline. The number of counts obtained is related to the concentration of the element in the sample, but no standards were used, so that absolute concentrations could not be calculated. The average value for the grains and range of values (in brackets) in counts per second, cps, are listed for a specified number of grains of each sample in Table XII. Ranges are given, since the error, which includes both analytical counting error and sample variation, could not be determined. One 50-second count on one grain of quartz yielded values (Ca = 6.1 cps, K = 4.2 cps, Na = 3.3 cps) which can be used to approximate background counts for these elements in everything but the microclines, which were analysed on a different day.

The results demonstrate that with heating, Na decreases and K increases in albite, and that K decreases and Na increases in the other minerals, while Si or Ca have remained constant. The range in K and Na counts in the heated minerals is much higher than in the unheated ones, indicating that the grains have undergone ion exchange to a variable extent. The extent of exchange that an individual grain has undergone, in all likelihood, depends on the environment of the grain in the rock, on its size and distance from grains with which it can exchange.

TABLE XII

Element X-Ray Counts for Heated and Unheated Minerals

Sample	No. of grains	Si (cps)	K (cps)	Na (cps)
Unheated biotite	8	229 (223-236)	347 (322-357)	4.3 (3.9-4.8)
1079 hour biotite	8	235 (221-257)	240 (155-299)	80 (48-116)
Unheated muscovite	5	300 (292-308)	386 (378-388)	26 (22- 32)
2.5 hour muscovite	5	304 (295-313)	384 (368-396)	25 (22- 28)
1079 hour muscovite	10	304 (293-320)	346 (303-369)	59 (38- 83)
		Ca (cps)	K (cps)	Na (cps)
Unheated albite	7	37 (18- 61)	6.9 (6.0-7.7)	524 (491-543)
2.5 hour albite	9	42 (16- 58)	8.4 (6.6-12.2)	512 (488-548)
1079 hour albite	10	49 (24- 63)	71 (12-342)	423 (218-512)
2.5 hour microcline	9	6.9 (5.8-8.1)	575 (554-583)	31 (23- 36)
1079 hour microcline	20	6.9 (5.8-8.8)	494 (417-555)	106 (55-179)

In the 1079 hour albite grains, large differences were observed also between the two counts obtained at different portions of the grain for every grain. For the 1079 hour microcline, there was no significant difference in the two counts for any of the grains, although different grains had exchanged K for Na to differing extents. For 1079 hour muscovite and biotite, in most cases the two counts within one grain were similar, although in a few grains a significant difference in the two counts was observable. The data demonstrate the presence of large concentration variations in the heated albites, some variation in the heated muscovites and biotites, and no variation in the heated microcline grains.

4. X-Ray Scanning Photographs

X-ray scanning photographs were taken of minerals in grain mounts (Plates I through V) and of the 405 hour thin section (Plates VI to VIII). Using the wavelength dispersive system on the electron microprobe, the spectrometers were set to detect the Kα x-ray wavelengths of certain elements, and photographs were taken with beam scanning over areas approximately 300 X 300 microns^2 (except for Plate V, where areas covered were approximately 37.5 X 37.5 microns^2). Each photograph is composed of dots, each dot or count referring to an x-ray quantum corresponding to the element of interest. The element and total number of counts obtained is listed for each photograph. Completely black areas in the grain mount photographs are epoxy in which the grains are mounted. Otherwise, the brightness (number of dots or counts) in different parts of a photograph varies with the concentration of the element being detected in the sample.

PLATE I

X-Ray Scanning Photographs of Microclines

1. 100 hour Microcline
   Na X 40,000 counts

2. 213 hour Microcline
   Na X 80,000 counts

3. 100 hour Microcline
   K X 90,000 counts

4. 213 hour Microcline
   K X 80,000 counts

PLATE I.

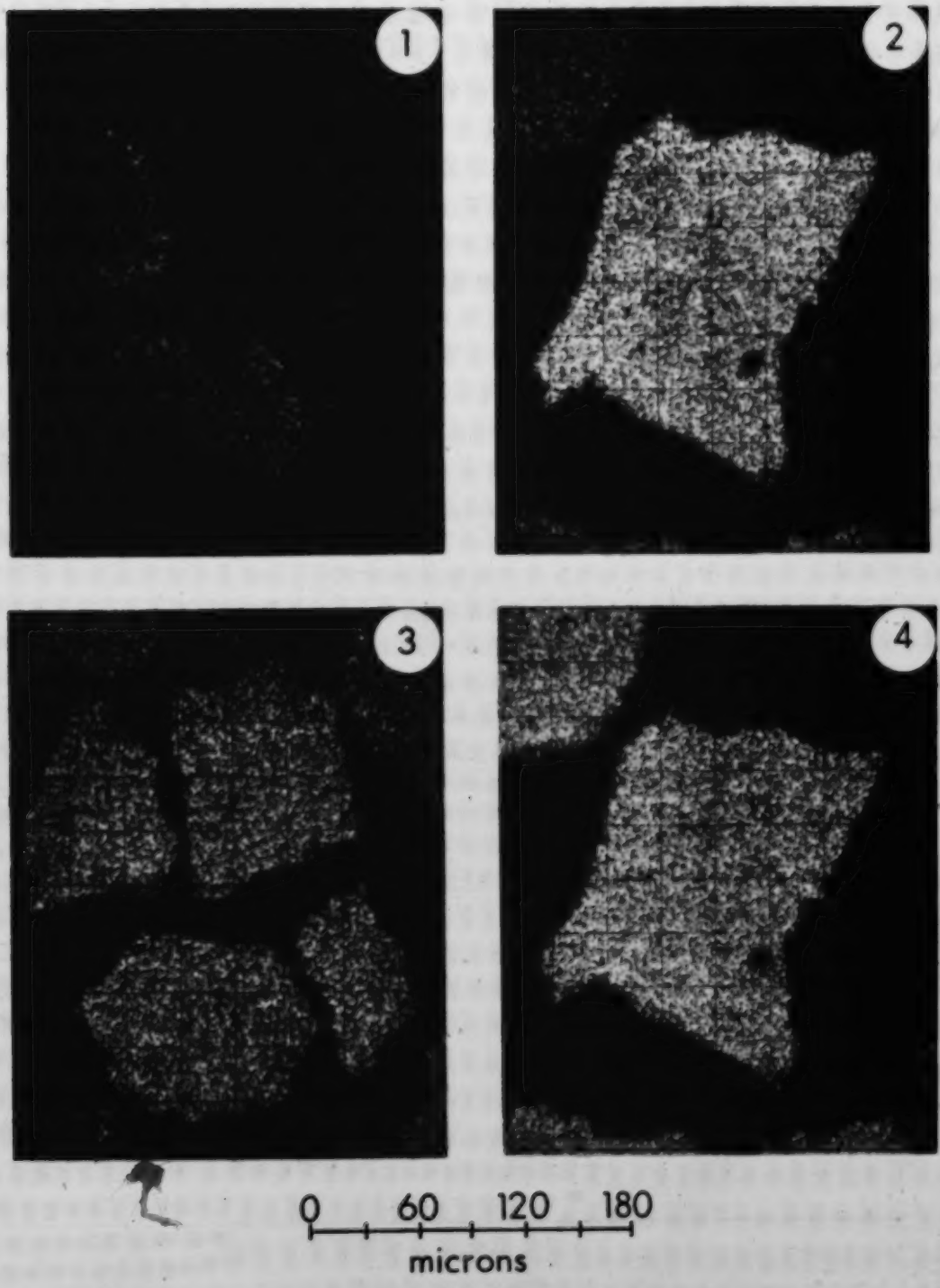

PLATE II

X-Ray Scanning Photographs of Albites

1. unheated Albite	2. unheated Albite	3. unheated Albite
Ca X 45,000 counts	Na X 80,000 counts	K X 80,000 counts
4. 2.5 hour Albite	5. 2.5 hour Albite	6. 2.5 hour Albite
Ca X 26,000 counts	Na X 95,000 counts	K X 60,000 counts
7. 100 hour Albite	8. 100 hour Albite	9. 100 hour Albite
Ca X 60,000 counts	Na X 80,000 counts	K X 60,000 counts
10. 1079 hour Albite	11. 1079 hour Albite	12. 1079 hour Albite
Ca X 80,000 counts	Na X 80,000 counts	K X 80,000 counts

PLATE II.

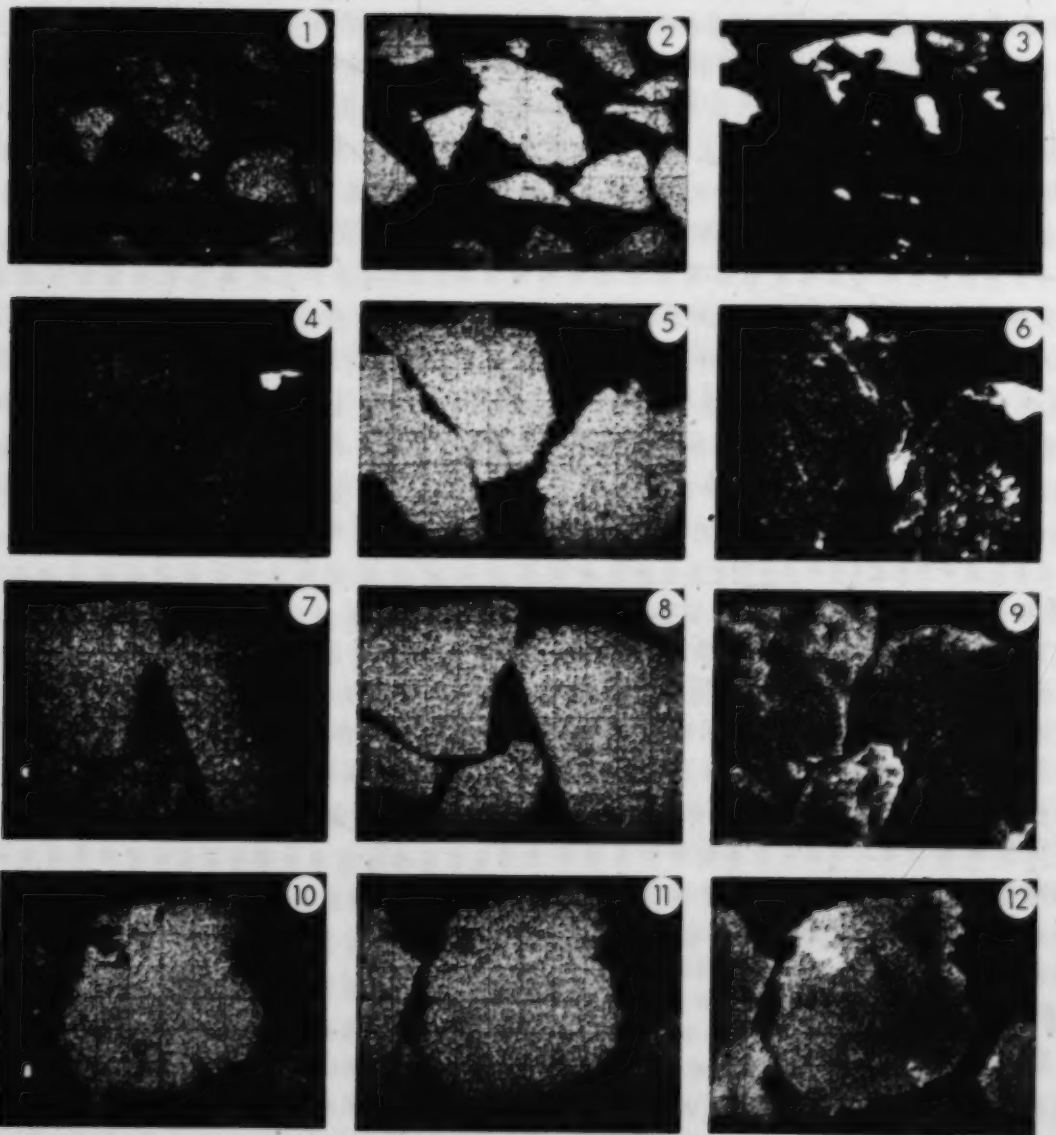

PLATE III

X-Ray Scanning Photographs of Muscovites

1. 100 hour Muscovite
   K X 70,000 counts

2. 100 hour Muscovite
   Na X 50,000 counts

3. 405 hour Muscovite
   K X 70,000 counts

4. 405 hour Muscovite
   Na X 60,000 counts

5. 1079 hour Muscovite
   K X 150,000 counts

6. 1079 hour Muscovite
   Na X 80,000 counts

PLATE III

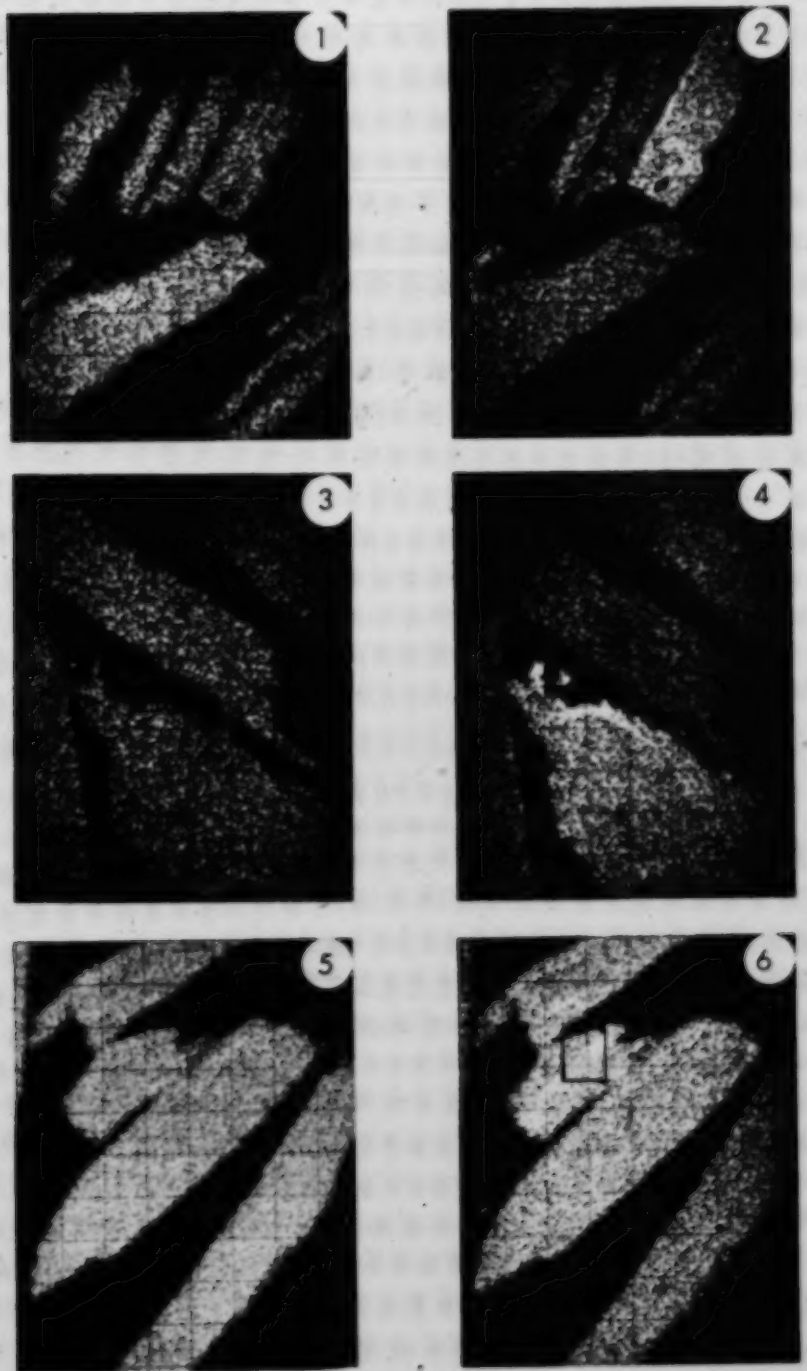

PLATE IV

X-Ray Scanning Photographs of Biotites

1. 100 hour Biotite
   Na X 50,000 counts

2. 1079 hour Biotite
   Na X 80,000 counts

3. 100 hour Biotite
   K X 70,000 counts

4. 1079 hour Biotite
   K X 80,000 counts

5. 100 hour Biotite
   Mg X 70,000 counts

6. 1079 hour Biotite
   Mg X 80,000 counts

PLATE IV.

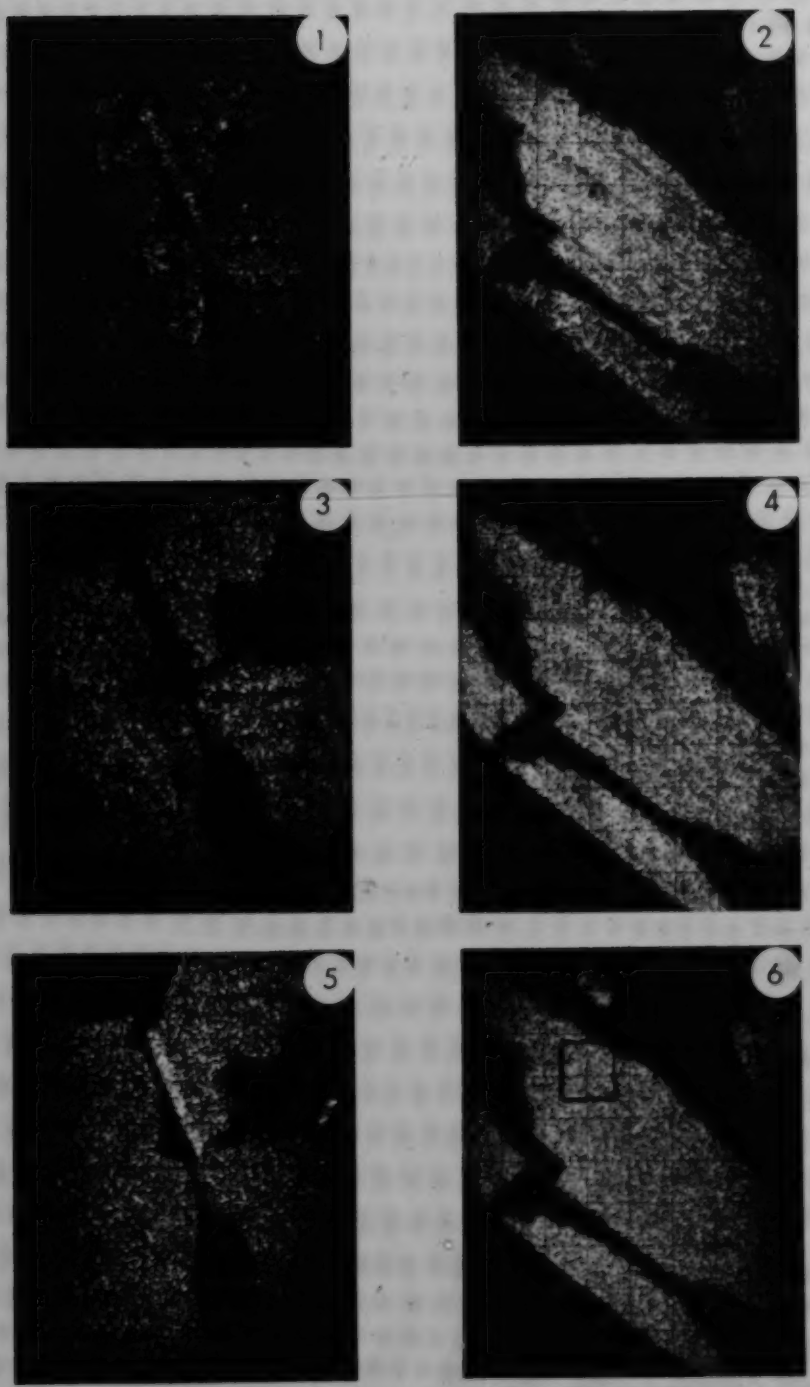

PLATE V

X-Ray Scanning Photographs - Enlargements*

of 1079 Hour Biotite and Muscovite

(all 80,000 counts)

1. 1079 hour Biotite Na

2. 1079 hour Biotite K

3. 1079 hour Biotite Fe

4. 1079 hour Biotite Si

5. 1079 hour Biotite Ti

6. 1079 hour Biotite Mg

7. 1079 hour Muscovite Na

8. 1079 hour Muscovite K

9. 1079 hour Muscovite Al

* Photographs 1 to 6 refer to the same area of 1079 hour Biotite indicated on Plate IV photograph 6; photographs 7 to 9 refer to the area of 1079 hour Muscovite indicated on Plate III photograph 6.

PLATE V.

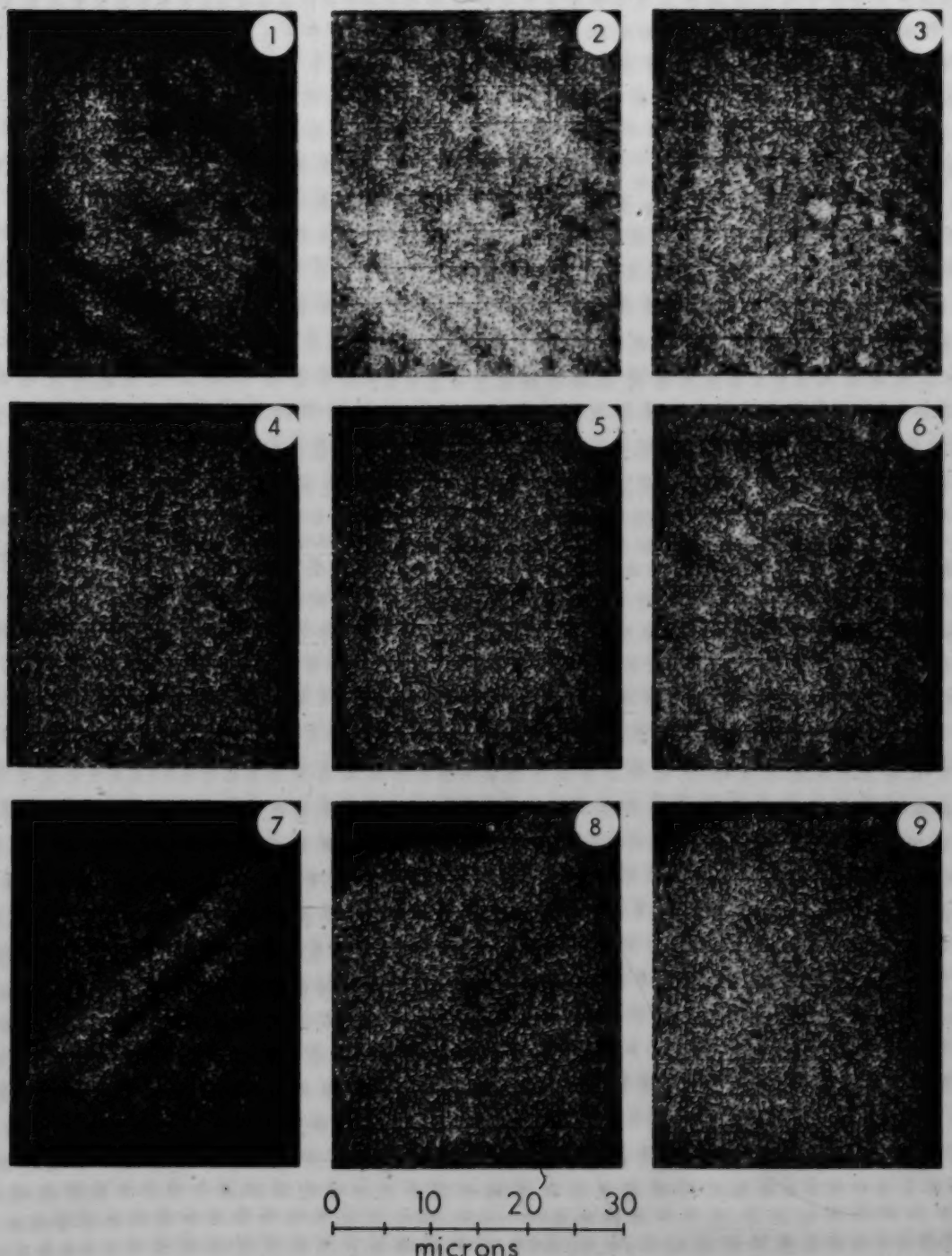

PLATE VI

X-Ray Scanning Photographs of 405 Hour Thin Section - Albite, Microcline Contact

(only albite and microcline are present in the field of view)

1. K X 80,000 counts

2. Na X 80,000 counts

3. Al X 80,000 counts

4. Ca X 40,000 counts

PLATE VI.

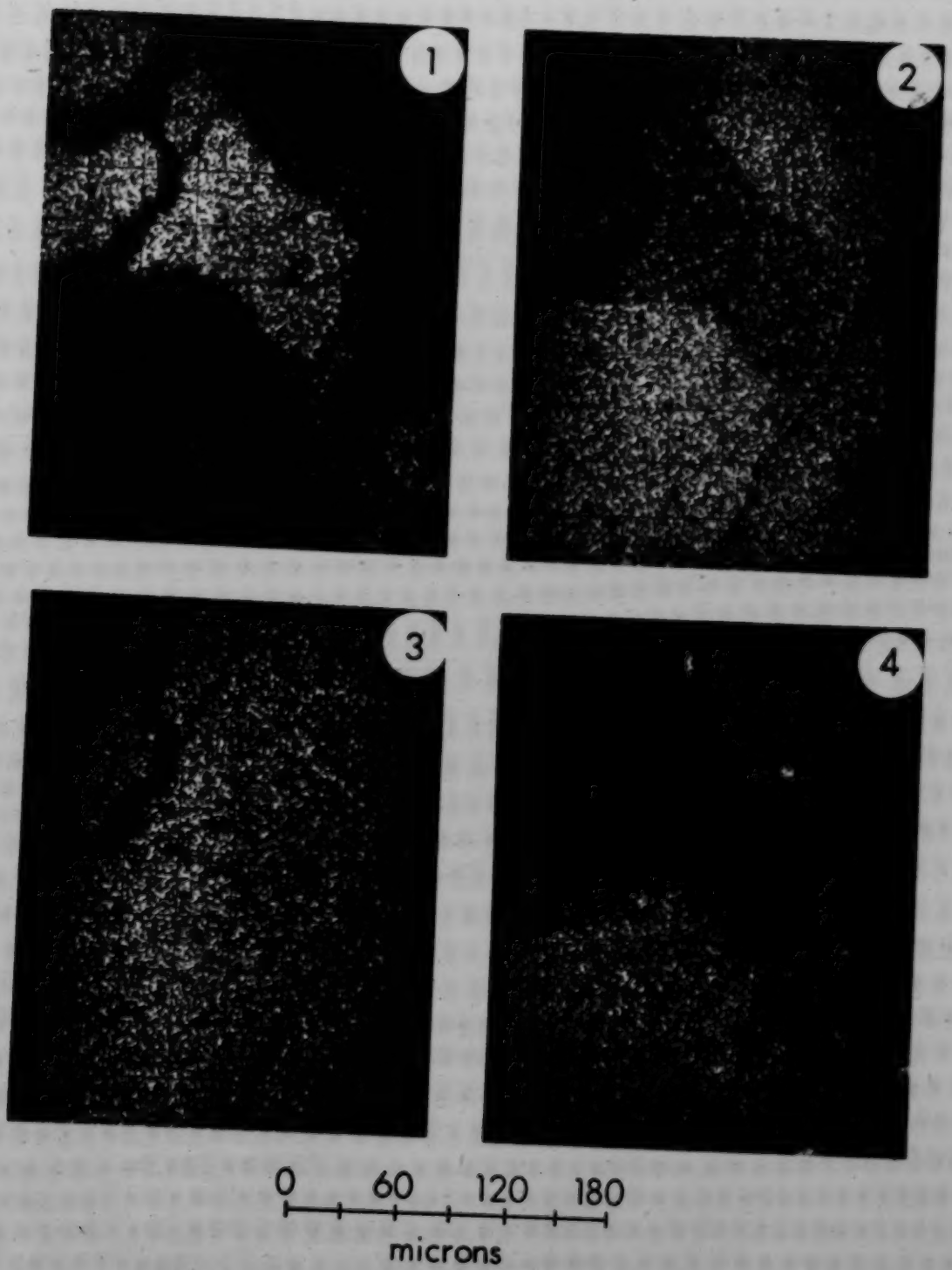

PLATE VII

X-Ray Scanning Photographs of 405 Hour Thin Section - Biotite, Albite, Quartz Contact

1. K X 70,000 counts

2. Fe X 70,000 counts

3. Na X 80,000 counts

4. Schematic diagram of thin section

Ab = albite

Bio = biotite

Qtz = quartz

PLATE VII.

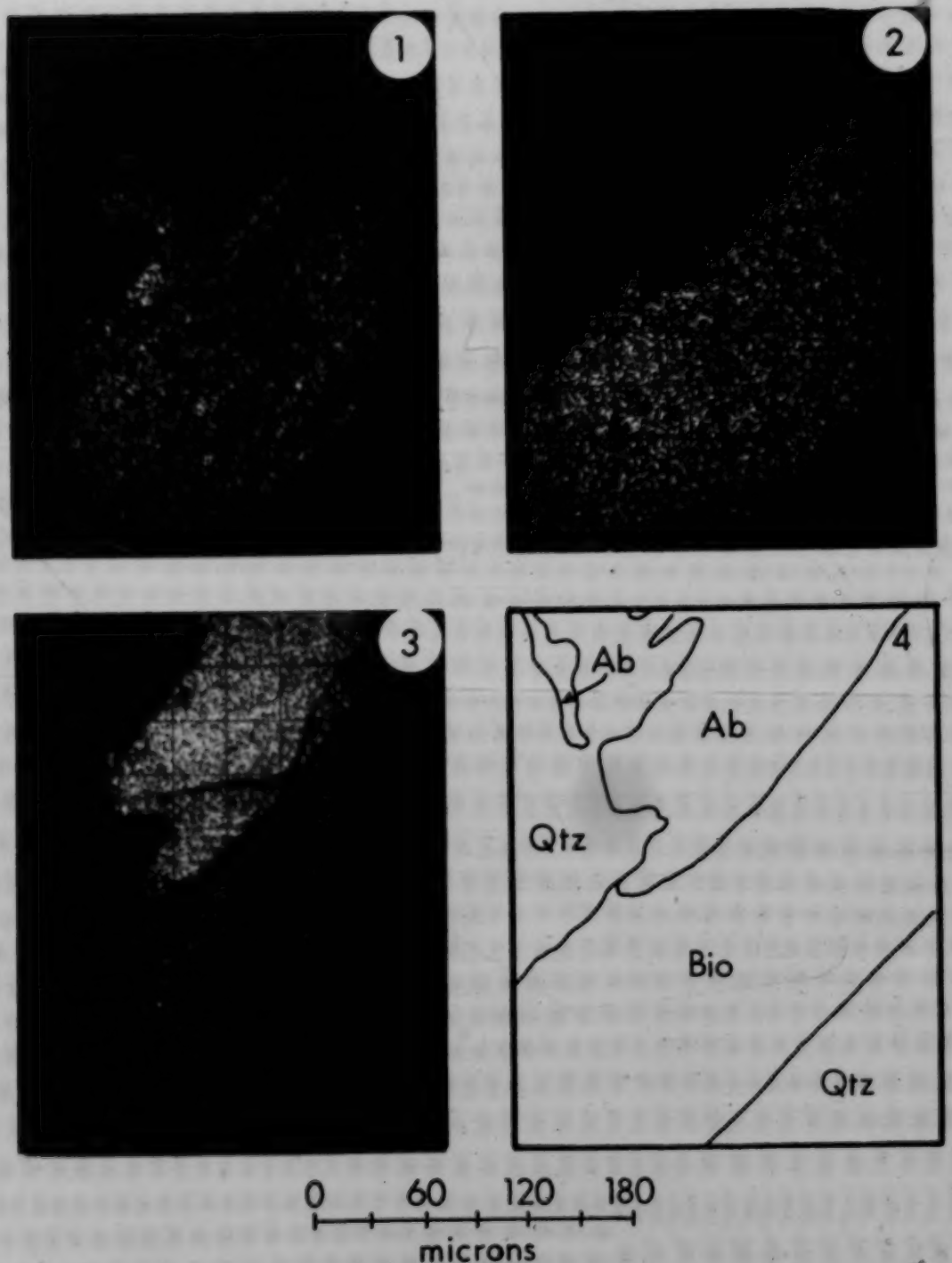

PLATE VIII

X-Ray Scanning Photographs of 405 Hour Thin Section -

Biotite, Albite, Quartz, Muscovite, Microcline Contact

1. Na X 70,000 counts

2. K X 70,000 counts

3. Al X 76,000 counts

4. Ca X 45,000 counts

5. Fe X 60,000 counts

6. Schematic diagram of thin section

Ab = albite
Bio = biotite
Qtz = quartz
Mic = microcline
Musc = muscovite

PLATE VIII.

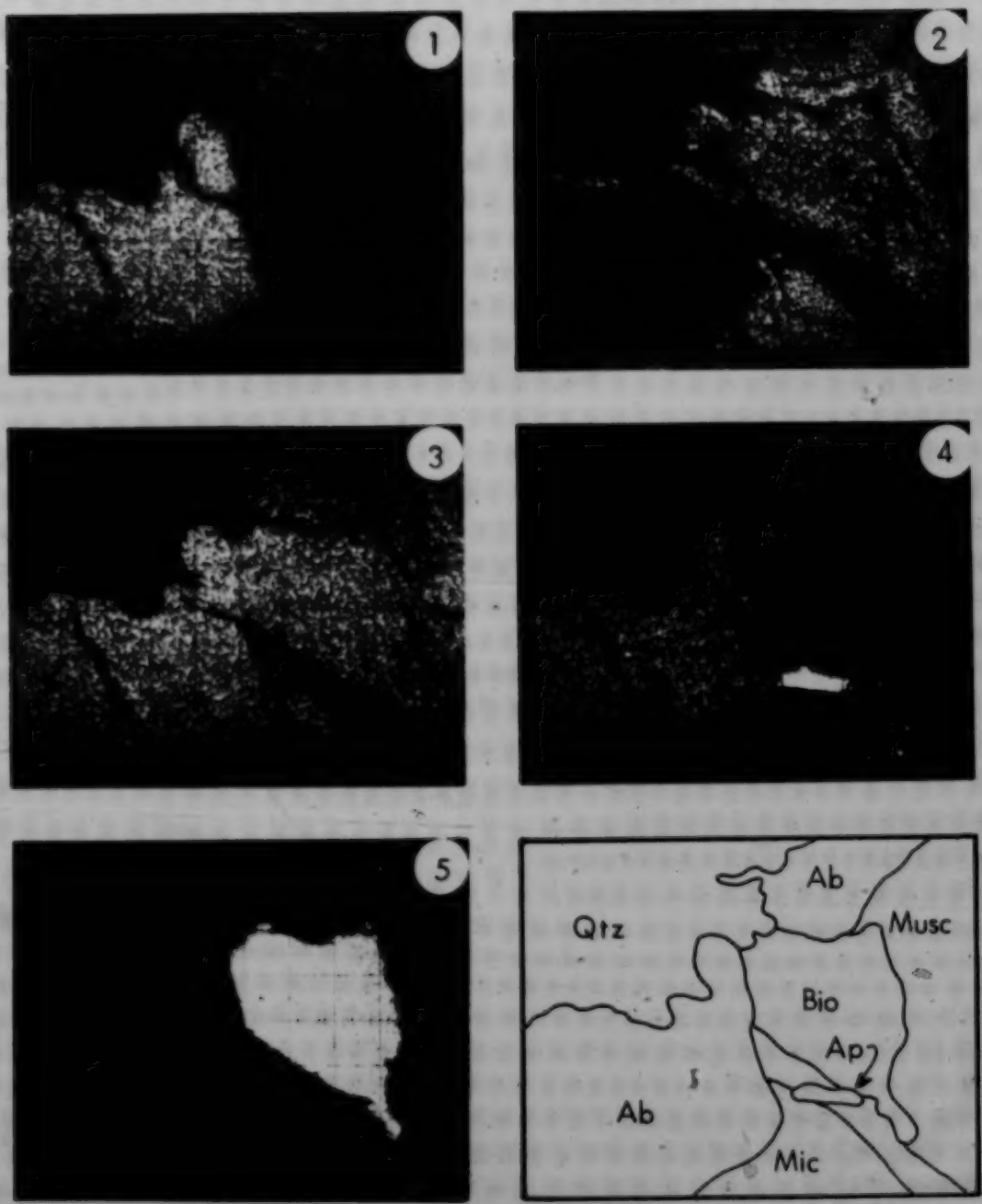

Plate I includes Na and K photographs of the 100 and 213 hour microcline samples. Some gradation of brightness can be seen in the Na photograph of the 100 hour microcline, i.e. there is a concentration gradient of Na within grains of microcline. A reciprocal variation of concentration in the K photograph cannot be seen due to the much higher concentration of K as compared to Na in the mineral. In the 213 hour photographs, no gradients of concentration are visible, but evidently there is still a variation in Na concentration between grains, although the difference does not show in the K photograph. (A change of Na concentration from, e.g. 0.1 to 0.2%, is very evident because twice the brightness results, whereas the corresponding change in K, e.g. from 8.0 to 7.9%, is not so easily visible since one region is 79/80th as bright as the other). Obviously, it will be difficult to detect any concentration gradients in the major elements of the minerals, therefore Na photographs for the K minerals, and K photographs for albite should be more closely inspected. In the microclines heated longer than 213 hours, no gradients or differences of Na or K concentration between grains could be detected by the photographic method. Unheated microcline was homogeneous with respect to K, and contained no Na, thus no photographs were taken.

Plate II details changes in Ca, Na, and K concentrations in albites from the unheated through to the 1079 hour sample. Very bright areas in the K photographs of unheated and 2.5 hour albite are impurities and inclusions of microcline. In the 100 and 1079 hour K photographs, sharp concentration gradients are evident, particularly around grain edges and near what was previously microcline. Reciprocal changes can be seen in the Na photographs. Ca photographs demonstrate some original inhomogeneity due to zoning of the plagioclase, but Ca does not appear to have

moved around with heating. The K photographs illustrate an increasing homogenization and smoothing of gradients with length of heating.

Plates III and IV of heated muscovites and biotites show some Na concentration variations within grains, and the biotites show analogous and opposite variations in K concentration. Areas of high Na concentration are not only at the edges of grains, but also appear in bands throughout a grain (perhaps parallel to the cleavage or along crystal imperfections?). Fe and Mg were homogeneously distributed in 1079 hour biotite and muscovite at the magnification of these photographs. Approximate areas where x-ray scanning photographic enlargements (seen in Plate V) of 1079 hour muscovite and biotite were taken, are outlined on photographs 6 of Plates III and IV.

Plate V again demonstrates reciprocal variations of K and Na in the 1079 hour muscovite and biotite. However, at the higher magnification, some localization of Fe and Mg concentrations in the 1079 hour biotite can be seen (not evident at the same magnification in unheated biotite), whereas Si and Ti are homogeneously distributed over the area of the photograph. The biotite photographs indicate the heat induced nucleation of new phases containing Fe and Mg, suggesting that these ions have migrated several microns from their original lattice positions. However, Na and K have exchanged over a larger scale, in a fashion apparently unrelated to the Fe and Mg distributions. There is no evidence of nucleation of new phases in the 1079 hour muscovite, since Al (and Mg) are homogeneously distributed, but nucleation could be occurring on a scale smaller than a few microns, and would not be visible on the photographs.

Plates VI to VIII are included to show that the same processes postulated to be occurring above, can also be visualized in the thin sections with the grains of the rock still in contact. Plate VI depicts

homogenization of Na and K between albite and microcline. The Ca photograph indicates the boundaries of the albite region, and that Ca has apparently not moved with heating. The K concentration gradients are haphazardly distributed around the microcline grain, suggesting that migration may be taking place along paths of least resistance, e.g. grain boundaries or crystal dislocations (non-volume diffusion as compared to volume or lattice diffusion).

Plates VII and VIII are generally self-explanatory. Black areas on all photographs are either cracks in the thin section, or quartz, which can be distinguished using the schematic diagram. These two plates demonstrate that indeed grain boundary or non-volume diffusion seems to be occurring to facilitate ion exchange in the rock. In Plate VII, cracks in albite can be seen in the Na photograph. Areas outlined by the cracks are precisely the ones which have gained the largest amount of K, as seen in the K photograph. Similarly, high concentrations of K can also be seen in Plate VIII along the contact between albite and quartz. The K must have moved from a K mineral by grain boundary diffusion to arrive at the above position. However, the central regions of albite grains, and areas further away from microcline have exchanged less of their Na for K than other regions (seen in Plates VIII and II), suggesting that volume diffusion is also occurring in the rock. Quartz appears to have behaved as an inert constituent during the heating experiment.

In summary, qualitative observations on the x-ray scanning photographs have resulted in the following conclusions. Na and K have interdiffused in the Prosperous Lake Granite between minerals over distances of tens to hundreds of microns as a result of heating.

Concentration gradients cannot be found in microcline heated longer than 100 hours, but very sharp concentration gradients exist in all the heated albites. The central regions of albite grains have undergone the least amount of ion exchange, suggesting a predominance of volume diffusion. Concentration variations found in the heated micas and 405 hour thin section are interpreted to signify that grain boundary diffusion, and migration along dislocations, cracks, or cleavage planes are also of importance in the rock. Ca, Al, and Si do not appear to have undergone any migration, nor Fe or Mg on scales comparable to the migration of K or Na. However, Fe and Mg in biotite have moved due to heating over distances of several microns (resulting in localizations of high concentration of these elements), implying the nucleation of new phases containing Fe and Mg due to instability of the biotite.

C. Powder X-Ray Diffraction Data on Unheated and Heated Minerals

1. Biotites

The samples of biotite selected for powder x-ray diffraction work were unheated biotite B, unheated biotite B mineral separate heated at 890°C for two hours, and the 5, 213, 802, and 1079 hour biotite samples. Data obtained for samples heated for 802 and 1079 hours were identical, as were results for the 5 hour sample and unheated biotite heated for two hours, therefore data for only one of each of these pairs are listed. Calculated d spacings and estimated intensities (I) of x-ray lines in the powder photographs are presented for the biotites in Table XIII (as well as hkl values for some biotite lines, assigned using ASTM biotite 2-45). Data on a sample of the Prosperous Lake Granite previously heated at 920°C for 100 hours (HB 920°C biotite; Baadsgaard and van Breemen, unpublished data) are also included for comparison in the table.

TABLE XIII POWDER X-RAY DIFFRACTION DATA ON BIOTITES

	Unheated Biotite		5 Hour Biotite		213 Hour Biotite		802 Hour Biotite		HB 920°C Biotite*	
hkl	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
001	10.06	100	9.88	100	9.88	100	9.84	100	9.88	10
	6.96	5	4.91	1	4.88	<1	4.62	1 br	4.74	5
020,110	4.59	10	4.56	10	4.55	8				
	3.90	1	3.94	<1					3.70	1
	3.66	7	3.62	10	3.61	10	3.65	20	3.66	20
	3.51	3							3.47	1
	3.39	10	3.35	10	3.35	10	3.33	3	3.32	1
003	3.34	40	3.29	70	3.28	40	3.28	30 } br	3.23	1
112	3.14	7	3.13	8	3.11	8	3.11	7 }		
113	2.91	7	2.88	8	2.87	10	2.87	7 } br		
	2.82	<1							2.89	10
	2.70	<1	2.67	<1	2.68	8	2.68	60	2.70	2
201,130	2.63	70	2.60	80	2.60	60	2.60	25	2.68	100
004,113	2.51	5	2.47	5	2.51	1	2.50	25		
					2.47	2	2.46	10 br	2.51	30
201	2.44	30	2.42	50	2.41	25	2.41	8	2.46	20 br
	2.41	<1								
	2.31	1	2.28	1	2.28	<1				
040,132	2.27	3 } br	2.24	3 } br	2.24	3				
							2.24	<1		
	2.18	25	2.16	50	2.15	20	2.20	10	2.20	15
							2.15	10 } br		
005	2.00	25	1.98	30	1.98	15	2.03	5 }	2.04	15 br
	1.91	2	1.89	3	1.89	3	1.98	5		
	1.85	<1	1.83	<1	1.83	2	1.89	<1		
	1.75	1	1.73	1	1.73	1	1.83	20	1.84	25
	1.70	1	1.69	1	1.69	5				
006	1.68	25	1.66	50	1.66	20	1.69	25	1.69	45
	1.65	<1					1.66	10		
	1.62	<1	1.61	<1	1.61	<1				
	1.59	<1	1.57	<1			1.59	3 } br	1.59	1
	1.54	50	1.53	70	1.53	50	1.56	3 }	1.57	4
	1.53	1	1.51	3	1.51	2	1.53	15 } br		
	1.48	2	1.46	2	1.48	1				
					1.46		1.48	15	1.48	25
					1.45	4 } br	1.45	20	1.45	30
	1.44	2	1.42	1	1.42	1	1.44	4		
	1.40	1	1.39	1	1.39	2				
	1.36	15	1.35	20	1.35	15	1.35	4		
	1.33	10	1.32	15	1.32	15	1.32	2	1.31	2
	1.31	5	1.30	7	1.30	7	1.30	8		
	1.30	5	1.29	7	1.29	7				
	1.27	2	1.26	2	1.26	1	1.26	2	1.26	1
	1.26	2	1.24	2	1.24	<1	1.24	1		
			1.23	<1						
	1.22	1	1.21	1	1.21	1	1.19	3	1.19	1
	1.20	1	1.19	1	1.19	1	1.16	3	1.16	2
	1.18	<1					1.14	5	1.14	2
	1.13	8	1.13	15	1.13	10	1.13	<1 br	1.10	2
	1.08	5	1.08	10	1.10	1	1.10	10		
	1.06	4	1.05	10	1.08	7			1.07	<1
					1.05	10	1.05	15	1.05	2
	1.05	5	1.04	10	1.04	10	1.04	3 br	1.04	1
	1.02	1	1.01	2	1.01	1	1.00	2 br		
	1.01	15	1.00	15	0.999	15				
	0.996	20	0.989	20	0.988	20	0.988	15 br		

br - broad or blurred together

* - lines due to hematite or spinel are underlined

The results on unheated biotite were compared with ASTM 2-45 biotite, and with biotite x-ray films in the X.R.D. library, University of Alberta. All lines, except weak ones at d spacings of 6.96, 3.51, 2.82 and 1.85 Å could be accounted for by biotite. The superfluous lines are not present in any spectra from the heated samples, and are probably due to slight contamination of unheated biotite with another phyllosilicate, e.g. chlorite.

In the 5 hour heated biotite, most of the x-ray diffraction pattern is preserved, but has been shifted to lower d values due to collapse of the biotite lattice after loss of water and oxidation of ferrous iron. Much of the structure is maintained in spite of heating to 1079 hours at 890°C, as evidenced by the intensities of lines in the x-ray spectra. However, by 213 hours of heating, there is significant appearance of new lines attributable to hematite (ASTM 13-534) and possibly spinel ($MgAl_2O_4$ - ASTM 21-1152), which increase in intensity in the 802 and 1079 hour samples. No new lines which can be assigned to other crystalline phases, e.g. silicates, can be found. In the HB 920°C biotite, lines due to biotite have virtually disappeared and the ones due to hematite and spinel predominate.

The above results are in accord with published work on heating biotites in air. The thermal stabilities of biotites vary greatly, since the number of octahedral vacancies varies, however, heating below approximately 600 to 700°C in air results in loss of hydroxyl protons (dehydrogenation) with simultaneous oxidation of Fe^{II} to Fe^{III} (Vedder and Wilkins, 1969; White and Sharp, 1971). Dehydroxylation also occurs, and "oxybiotite", which has a unit cell contracted along the c-axis (decreased d_{001}) as compared to unheated biotite, is formed (Wones and

Eugster, 1965). The oxybiotite structure is unstable, and with heating to higher temperatures, delamination and structural breakdown occur, with the ejection of octahedral Fe^{III} and formation of hematite, both interlayer and along cracks, dislocations, holes and crystal surfaces. Heating for longer times or at higher temperatures results in the formation of an increasing amount of hematite. Depending on the conditions of dehydration, olivine, magnetite, leucite or other crystalline phases can be found on heating lepidomelane; often new phases are amorphous or poorly crystalline (Akizuki et al., 1975).

According to Schneider (1974), intersheet and octahedral layers of biotite decompose more readily on heating than individual $(Si,Al)O_4$ tetrahedra, and crystallization of iron oxides occurs before that of silicates also because of differences in ionic mobility and energy of nucleation of various phases. The only new crystalline phases detected in heated biotite from the Prosperous Lake Granite were hematite and spinel (plus the oxybiotite structure which persisted even at 1079 hours). Thus, x-ray diffraction results and electron microprobe x-ray scanning photographs in the present experiment confirm the occurrence of the decomposition processes described above during heating of biotite in situ in a rock.

Undoubtedly, the ready decomposition of biotite on heating accelerates the K-Na exchange between biotite and albite in the Prosperous Lake Granite. Not only is the lattice unstable, but also many crystal imperfections and nucleation sites, where rapid diffusion could occur, are created due to dehydration and oxidation of biotite. Although oxidation of ferrous iron can be compensated by the loss of interlayer cations, e.g. K^+ (Farmer et al., 1971), in the present case

charge compensation has occurred rapidly via loss of protons (see Experimental Procedures - Heating of Mineral Separates). Only exchange of Na for K in "oxybiotite" occurs with heating; there is no net loss of interlayer cations (Microprobe Results, section B.1). In previous sections, the migration of Na, Rb, and Sr^{87r} in biotite was found to be about ten times as rapid as for the same cations in muscovite and microcline, probably because of the instability of the oxybiotite structure. The calculated diffusion coefficients may perhaps be applicable to cation diffusion in oxybiotite, however, probably signifying to a large extent non-volume diffusion processes. It is unreasonable to assume that the same processes necessarily occur in biotites within the stability field of biotite. At best, the diffusion coefficients calculated in this study put an upper limit upon how rapidly cations can diffuse through biotite, considering solid state processes only (i.e. no dissolution, reprecipitation reactions).

2. Muscovites

The unheated muscovite B, the same unheated muscovite heated at 890°C for two hours, and the 5, 50, and 1079 hour muscovite samples were chosen for powder x-ray diffraction study. The unheated muscovite heated for two hours and 5 hour muscovite yielded the same results, thus only data for 5 hour muscovite are reported. Results on the above samples and on HB 920°C muscovite (muscovite from the Prosperous Lake Granite heated at 920°C for 100 hours; Baadsgaard and van Breemen, unpublished results) are shown in Table XIV.

TABLE XIV POWDER X-RAY DIFFRACTION DATA ON MUSCOVITES

	Unheated Muscovite		5 Hour Muscovite		50 Hour Muscovite		1079 Hour Muscovite		HB 920°C Muscovite*	
hkl	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
003	9.99	75	9.99	10	9.99	10	9.99	8	9.99	5
006	4.98	5	5.00	10	5.00	10	5.00	6	5.00	5
100	4.46	75	4.48	100	4.48	100	4.50	100	4.51	50
113	4.31	1	4.29	1	4.30	1	4.31	1	4.25	5
023	4.11	1	4.14	1	4.14	1	4.15	<1		
104	3.88	10	3.89	30	3.88	30	3.89	25	3.94	3
	3.72	10	3.75	30	3.75	30	3.76	25	3.81	3
116	3.49	15	3.50	30	3.49	30	3.50	25	3.51	5
009	3.33	75	3.35	85	3.34	80	3.35	70	3.36	100
116	3.19	15	3.20	20	3.21	20	3.22	20	3.23	20
	2.99	20	3.01	20	3.02	15	3.01	15	3.04	5
108	2.86	15 br	2.87	20	2.87	15	2.88	15	2.89	5
	2.79		2.81	2	2.80	2	2.80	3	2.82	2
111	2.57	100	2.58	70	2.59	70	2.59	60	2.59	20
00,12	2.46	5	2.50	5	2.50	5	2.50	3	2.52	1
	2.38	10	2.40	10	2.40	8	2.41	10	2.46	1
200	2.24	3	2.25	20	2.25	20	2.26	20	2.40	20
	2.20	1							2.27	3 br
118	2.13	15	2.15	7	2.16	7	2.15	4	2.15	2
	2.06	1	2.08	3	2.08	4	2.09	4	2.10	1 br
00,15	2.00	15	1.99	20	2.00	20	2.00	20	2.00	20
11,10	1.95	1	1.95	<1	1.96	<1	1.96	<1		
11,11	1.88	1	1.89	2	1.90	2	1.90	2	1.90	1
	1.82	1	1.84	<1			1.85	1	1.82	3
	1.73	3	1.74	1	1.75	1	1.74	1		
	1.70	1	1.71	3	1.72	3	1.72	2		
11,14	1.65	10 br	1.66	20	1.66	20	1.66	20	1.67	10
	1.60	2	1.62	3	1.62	3	1.62	4		
	1.55	2	1.56	7	1.56	6	1.57	8		
	1.52	2	1.53	5	1.53	3	1.53	8	1.54	10
300	1.50	20	1.51	7	1.51	6	1.51	8	1.51	2
	1.45	1	1.46	1	1.47	<1	1.47	1		
	1.43	1	1.44	2	1.43	1	1.44	1		
	1.35	4	1.36	7	1.36	5	1.41	3	1.41	15
	1.34	1	1.35	<1	1.35	1	1.36	4	1.38	3
			1.33	1	1.33	1	1.35	1 br		
	1.29	5	1.31	5	1.31	5	1.33	1		
			1.30	1	1.30	1	1.31	5		
			1.29	3	1.29	2 br	1.29	2 br	1.29	1
	1.27	1	1.27	1	1.27	1				
	1.25	5	1.25	10	1.25	7	1.27	<1	1.26	2
	1.22	2	1.22	<1	1.22	1	1.25	6	1.23	2
							1.22	<1		

br - broad or blurred together

* - lines due to quartz or γ-Al_2O_3 are underlined

Miller indices assignments for muscovite were made using reported hkl values for a natural 3T muscovite (ASTM 7-42).

The unheated muscovite data compare favorably with spectra in the ASTM catalogue (e.g. synthetic muscovite $2M_1$, ASTM 7-32, and natural muscovite 3T, ASTM 7-42). Essentially all lines persist with the same position and intensity in all samples of muscovite heated at 890°C. There is a slight change in intensity going from unheated to heated samples, mainly in d_{001} lines, probably as a result of changes in the x-ray diffracting power of the lattice due to water loss. There may be a small increase in d spacings (expansion of the lattice) with heating. There are two lines of low intensity in the 1079 hour muscovite spectrum at 1.53 and 1.41 Å which differ from spectra of the shorter heated samples. The lines can also be seen in the HB 920°C muscovite, in which the muscovite pattern has become much less intense and a new spectrum which can be assigned to α-quartz (ASTM 5-490) and γ-alumina (ASTM 10-425, with a spinel structure, includes lines at 1.53 and 1.41 Å) or spinel (ASTM 21-1152) is emerging.

Apparently muscovite in the present heating experiment has retained the three dimensional structure of dehydrated muscovite with heating for long periods of time at 890°C. The dehydrated muscovite does not appear to have undergone significant decompositon, although a small amount of an aluminous spinel phase may be present in the longest heated samples. In the x-ray scanning photographs, no nucleation of new phases was detected, suggesting that dehydrated muscovite is quite resistant to structural breakdown.

Roy (1949) found no marked changes upon heating muscovite in air to 940°C. Above this temperature structural breakdown occurred,

resulting in the formation of γ-alumina or spinel. Around 1400°C, corundum, α-Al_2O_3, rather than γ-AL_2O_3 (which also contains some Si) formed. Dehydroxylation above 600°C has been found to proceed rapidly due to marked delamination or exfoliation of the mica into thinner sheets, resulting in some puckering of the lattice as well as expansion along the c-axis (Vedder and Wilkins, 1969).

The most extensive heating experiments on muscovite have been carried out by Eberhart (1963 A, B), who obtained similar findings to the above workers. During dehydration (dehydroxylation) the configuration of octahedral and interlayer cation sites were perturbed. Structural breakdown to γ-Al_2O_3 ("spinel") occurred around 1000°C, with other phases, e.g. mullite, leucite, tridymite, forming at higher temperatures. By electron diffraction, however, small crystals (approximately 0.1 micron) of spinel were found to begin appearing with heating at approximately 800°C. The spinel crystals had a definite orientation with respect to the muscovite lattice, and formed more readily along cracks, crystal defects, and cleavage planes. Spinel also formed more easily in muscovite with a higher Na content.

According to Franz and Althaus (1976), substitution of Na for K is a common solid solution mechanism in K micas. Up to 30% of the K in muscovite can be replaced by Na randomly in solid solution without change (decrease) in the lattice spacings, since the large K ions hold apart the interlayer sheets (Nicol and Roy, 1965). Greater than 30% Na substitution puts more strain on the aluminosilicate framework and usually results in an intergrowth of Na- and K-containing phases. It thus appears that incorporation of Na into muscovite, although possible, destabilizes the structure and leads to more rapid breakdown.

X-ray diffraction results for both muscovites and biotites from the Prosperous Lake Granite did not demonstrate any decrease in d spacings due to substitution of increasing amounts of Na into the structure with heating (over 30% exchange did not occur in either case). In addition, the dehydrated muscovite has not decomposed significantly, or has undergone structural reorganization only on a submicroscopic scale in this experiment.

As with biotite, the dehydration of muscovite must increase the rate at which K-Na exchange occurs with heating due to delamination and the creation of many new diffusion paths. Also, x-ray scanning photographs demonstrate little variation of concentration throughout muscovite grains, suggesting non-volume diffusion to be the main process operative. Calculated diffusion coefficients for K-Na exchange in muscovite (Microprobe Results, section B.1) thus may apply for non-volume diffusion in dehydrated muscovite, where diffusion is probably faster than for the same cations in a stable muscovite.

The results of section A.2 indicated an increase in Rb in muscovite with increased heating time, although Sr^{87r} and K decreased. At 890°C the structure of dehydrated muscovite, which is slightly expanded along the c-axis, is probably the only one that can accomodate the larger Rb ion that is being lost by biotite. Beswick (1973) has found at two kbar total pressure, above 700°C, complete solid solution of Rb in K-phlogopite whereas the solid solution of Rb in sanidine was very limited. At the higher temperatures employed by Baadsgaard and van Breemen (1970), Rb as well as K and Sr^{87r} in muscovite was found to decrease with increasing temperatures. However, at these temperatures, the muscovite structure was more completely decomposed to γ-Al_2O_3 and quartz, phases

which would tend to exclude Rb.

3. Albites and Microclines

The feldspar mineral separates had not been totally purified and detailed powder x-ray diffraction work was not carried out. However, visual comparison of x-ray films on unheated and 1079 hour microcline indicated preservation of all lines in the 1079 hour film with a shift to shorter d spacings, believed due to the incorporation of Na into the microcline. Comparison of unheated albite and HB 920°C albite (heated at 920°C for 100 hours; Baadsgaard and van Breemen, unpublished results) films also indicated conservation of the albite structure with heating, although with some blurring of lines, probably due to a variable degree of substitution of K for Na.

Both albite and microcline have likely undergone a slight degree of (Al, Si) disordering by 1079 hours at 890°C. Although rates of disordering of alkali feldspars vary, the process is very slow under dry conditions except at temperatures near the melting point of the mineral. For example, McKie and McConnell (in The Feldspars, 1974, Vol. 1, Smith, ed.) found that the Amelia albite underwent only about 30% of the maximum possible disordering during dry heating for approximately 1000 hours at 920°C. In the present experiment, the cross-hatched and monoclinic twinning of microcline and albite were retained in the heated samples, suggesting a still ordered structure for these minerals.

Albite and microcline do not appear to have decomposed during the heating experiment, although some structural rearrangement, i.e. disordering, may have occurred. Since these minerals contain no water, heating has not disrupted the lattices significantly into mosaics, and

thus alkali ion exchange between the feldspars probably occurs mainly via volume diffusion.

SUMMARY AND CONCLUSIONS

When the Prosperous Lake Granite (a quartz monzonite) was subjected to heating in air at 890°C for varying periods of time up to 1079 hours, substantial relocation of alkali (Na, K, Rb) and strontium ions between minerals was found to occur. A combination of Rb/Sr isotopic and electron microprobe techniques was used for analysis. Potassium was lost from all the K-minerals (biotite, muscovite, microcline) with a commensurate gain in sodium. Sodium was lost and an equivalent amount of potassium gained by albite. Thus, alkali ion exchange occurred between the K- and Na-minerals in the rock. Rubidium and radiogenic strontium were found to decrease in heated biotite, whereas rubidium increased and radiogenic strontium (possibly also normal Sr) decreased in heated muscovite. There was no net change in the concentrations of any other elements in any mineral with heating.

An idealized diffusion model (for diffusion out of or into a semi-infinite medium) was applied to analyse the concentration-time data, resulting in plots of concentration versus square root of time for the previously mentioned elements in each mineral. The plots should be linear if the diffusion model is applicable and if the ionic migrations are diffusion controlled. In fact, all the concentration versus square root of time data were observed to adhere to a linear relationship relatively well, except those for Rb and Sr^{87r} in muscovite (where there was no concentration change up to approximately 100 hours, after which the concentration versus square root of time plots appeared to show a linear increase or decrease). Diffusion coefficients were calculated from the slopes of the linear portions of the curves, assuming diffusion out of an infinitely thin plate, and the effective dimension for dif-

fusion to equal the average mineral grain size. The values obtained for diffusion coefficients, D, varied from 10^{-15} to 10^{-12} cm^2/sec, with the highest values for loss of K, Rb, and Sr^{87r} from biotite, intermediate values for loss of K and Sr^{87r} and gain of Rb by muscovite and loss of K from microcline, and lowest values for loss of Na by albite. The values for different elements in a given mineral (biotite or muscovite) did not vary by more than a factor of five. The calculated diffusion coefficients were of comparable magnitude to results cited in the literature for diffusion of the alkali ions, Na, K, and Rb in pure mica and feldspar minerals.

Since Na or K loss from the minerals occurred via a process of ion exchange, the calculated coefficients for Na or K diffusion were actually interdiffusion, not self-diffusion, coefficients. From considerations of interdiffusion in section B.2 of Results and Discussion, exchange of Na and K appeared to be determined by the diffusivity of the less mobile ion, K. In particular, the diffusion coefficient calculated for the loss of Na from albite was probably equivalent to a self-diffusion coefficient for K in albite. Coefficients calculated for loss of K by the K-minerals would have referred to interdiffusion coefficients, intermediate in value between the self-diffusion coefficients of Na and K in these minerals. The coefficients calculated for Rb and Sr^{87r} migration in the micas were probably similar to self-diffusion coefficients, since these elements were present in trace concentrations in the minerals.

Qualitative information on Na and K relocation was obtained from electron microprobe work using wavelength dispersive analysis and x-ray scanning photography. These methods illustrated that the heated mineral grains had exchanged Na for K (or vice versa) to variable extents,

probably determined by grain size and the environment of the grains in the host rock. Also, sharp concentration gradients in a radial distribution were found in all the heated albites, but no gradients in microcline heated longer than 213 hours could be seen. X-ray diffraction indicated no decomposition of albite or microcline, minerals which could be expected to be stable under the conditions of the heating experiment. Apparently, volume diffusion, and the mobility of the larger cation, K, mainly governed ion exchange between the two feldspar minerals.

X-ray scanning photographs of heated muscovites and biotites did not exhibit Na and K concentration variations in a pattern which could be correlated to volume diffusion. Some areas of high Na concentration in bands through grains, along cracks and grain boundaries, suggested the importance of non-volume diffusion in the mica minerals. In photographs of heated biotite, Fe and Mg were found to have localized and concentrated in blebs on a scale of a few microns. However, there was no change in the homogeneous distributions of elements, e.g. Si and Al, and no relation of the Fe and Mg variations to Na and K concentration distributions.

Powder x-ray diffraction work was carried out on the heated and unheated micas. In conjunction with the x-ray scanning photographs, the results indicated that heated biotite had significantly decomposed to hematite, the amount of hematite formed increasing with increasing duration of heating. However, much of the dehydrated biotite (oxybiotite) structure was also retained up to the longest heating time. The dehydrated muscovite structure appeared to be more stable to thermal destruction, and only in the longest heated samples was there any

evidence of slight decomposition to γ-alumina or spinel.

In summary, Rb, Sr^{87r}, Na, and K ions migrated between minerals, on scales approximately equal to the grain size, upon heating of the Prosperous Lake Granite. Other elements remained stationary, or, in the minerals undergoing decomposition (micas), Fe, Mg, and Al moved only over distances of a few microns or less. The experiment was conducted under almost completely anhydrous conditions. Thus, all migration must be accounted for by solid state migration (volume or non-volume diffusion), with no contribution from movement through intergranular water or dissolution-reprecipitation reactions. At least two of the constituents of the rock, biotite and muscovite, decomposed to some extent during the experiment.

Difficulties arose in quantifying the rates of migration of the above ions, due to sample variability and contamination because of inability to completely separate the minerals. Although, on the basis of theoretical considerations, a diffusion model was chosen, most of the scattered concentration data would have fit a first order or zero-order rate model equally well. A rate controlled reaction, e.g. in particular, decomposition of muscovite or biotite, could therefore control the rate of release, acceptance, and migration of an ion in the rock, or at least within that mineral. However, muscovite did not significantly decompose during the experiment, making rate control by decomposition unlikely. Diffusion in the micas was probably speeded up by the creation of new diffusion paths where non-volume diffusion could occur due to dehydration. In light of the complications, it is actually surprising that the "diffusion coefficients" calculated in the experiment were so similar to values obtained by other workers studying the dif-

fusion of ions in stable minerals.

In simplified terms, the diffusivity of ions in a given lattice should decrease with increasing ionic size and charge, if the effect of water is ignored. The results of this thesis support the above statement, in that except for Sr^{87r}, only the monovalent alkali cations underwent migration on significant scales in the heating experiment. Higher charged cations moved only on a submicroscopic scale (Fe, Mg) or apparently not at all (Ca, Si). However, the divalent Sr^{87r} ion relocated as much as the alkali ions, whereas Ca, Mg, and Sr^{N} did not. Evidently, the phases involved in ion exchange, the ions moving, and thus the migration rates observed, cannot depend on only diffusion rates and kinetic factors. Thermodynamic factors must also exert a great deal of control.

For example, what could be expected to happen if a rock whose minerals were in chemical and isotopic equilibrium at the time and under the conditions of its formation was later reheated? If the conditions of formation and reheating were similar, the equilibrium should not be disturbed; no matter how rapid the diffusion, e.g. of K ions, re-equilibration should result in concentrations the same as present initially. For radiogenic nuclides the situation is different. These nuclides accumulate with time due to decay of their radioactive parents, and are trapped in sites in minerals which are usually geochemically and thermodynamically unfavorable. Thus, on reheating of a rock, there is a driving force for radiogenic isotopes to re-equilibrate by migration even if other elements are still in equilibrium between minerals. Such are the processes assumed to result in diffusive loss of radiogenic nuclides with metamorphism.

If a rock is subjected to conditions different (especially more strenuous conditions) from the original equilibrium, other changes tending in the direction of a new equilibrium, will also occur. At higher temperatures, because of shifts in equilibria, increasing substitution of K for Na, or Na for K can result, to the extremes seen in the present experiment, but also under geologic conditions, e.g. Lambert (1959, in Deer, Howie, and Zussman, 1962) found that the Na contents of muscovites increased with metamorphic grade.

In the present experiment, a situation very much perturbed from normal geological conditions was produced. Some minerals were grossly destabilized and began to decompose. Schneider (1974) found that biotites from granitic rocks around a crater impact had partially oxidised and decomposed to oxybiotite and iron oxides, with a diffusion of K out of, and Ca and Na into the lattice. However, under most metamorphic conditions such processes would only occur to a minor degree. At the lower temperatures usually considered when evaluating too low radiometric ages, alkali ions would not be expected to relocate significantly, not because of diffusive and kinetic factors, but because of equilibrium considerations and limited solid solution of these ions for each other in minerals.

Examining data from the present experiment, it is apparent that radiogenic strontium has been lost by the mica minerals, as would occur under metamorphic conditions, and that the alkalis have migrated due to the very high temperatures employed. Because of decomposition of minerals, and the disequilibrium conditions to which the rock was subjected, the results of this thesis cannot be interpreted to yield quantitative data on the diffusion of geochronologically important nuclides. The

present experiment, albeit at the extremes of geologic reality, has indicated that atomic relocation in a rock is affected by a summation of kinetic and thermodynamic factors, which may be inseparable. From both the investigator's and investigatee's points of view, only time will tell.

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APPENDIX

A. Experimental Techniques

1. Isotopic Analysis for Rubidium and Strontium

Rb and Sr determinations were carried out on heated and unheated muscovites and biotites and on the unheated microcline samples by the method of isotope dilution or "spiking".

Enough sample estimated to contain approximately 20 microgram of Rb was decomposed by heating in a platinum crucible using 5 ml. vapour distilled HF, 5 ml. demineralized distilled water, and 5 drops of concentrated H_2SO_4. About 20 microgram of almost pure Rb^{87} spike was added and equilibrated with the sample, which was then evaporated to dryness and ignited at 900°C. The residue was leached with distilled water, and the potassium and rubidium were precipitated by the addition of "suprapur" concentrated $HClO_4$. The precipitate was redissolved in a few drops of distilled water in preparation for mass spectrometric analysis.

In the analytical procedure for strontium, enough sample was weighed to give approximately 20 microgram of normal (non-radiogenic) Sr. The sample was decomposed by heating in a teflon beaker with 10-15 ml. each of pure vapour distilled concentrated HNO_3 and HF. A spike containing 20 microgram of almost pure Sr^{84} was added and equilibrated with the sample. The solution was evaporated to dryness and the residue taken up in a mixture of HNO_3 and water, and redried several times. Strontium was collected from a concentrated HNO_3 solution of the sample by coprecipitation with $Ba(NO_3)_2$, after the addition of strontium-free barium solution (approximately 10 mg. total Ba was added). The washed precipitate was dissolved in HCl and placed onto a pre-calibrated Dowex

cation exchange column, which was eluted with 2.5 M. vapour distilled HCl. The eluate fraction containing Sr was collected and evaporated to dryness. The residue was dissolved in a few drops of distilled water to load it onto filaments.

Both Rb and Sr were loaded onto previously outgassed tantalum filaments. For all of the strontium and some of the rubidium work, single tantalum filaments were used. The filament was oxidized by passing a current through it, and small amounts of Rb or Sr containing solution were added and evaporated under a heat lamp until a residue was built up on the filament. Sr on the filament was treated with $HClO_4$ for ultimate conversion to the oxide form, and Rb with H_2SO_4 for conversion to the sulfate. Most of the Rb samples were re-analysed using triple filaments of tantalum. The Rb was loaded as one or two large drops onto the unoxidized center filament, and evaporated to Rb chloride; it was not converted to the sulfate salt. The side filaments were used for ionizing the sample.

The samples, after loading onto filaments, were analysed on a six-inch solid source mass spectrometer, utilizing peak switching and digital voltmeter output. A 3.5 kV. accelerating voltage was used, and for single filament Sr and Rb runs, currents of approximately 2.4 and 1.3 amperes, respectively, were needed to ionize the samples. For triple filament Rb analyses, 0.4 amps. on the center (sample) filament and approximately 2.3 amps. on the side (ionizing) filaments were the operating conditions employed.

Peak switching data were converted to isotopic ratios by calculation of a running mean on the closely linear digital output. Several sets of data were collected and averaged, if possible. An APL

program, RBSRCOM, written by Dr. Baadsgaard, was used to calculate the Rb and Sr contents and isotopic composition of the samples, given sample weight, isotopic ratios in the spiked sample, and spike quantity and composition as input.

All Sr isotopic data were corrected for fractionation by normalizing ratios to $Sr^{86}/Sr^{88} = 0.1194$. The Eimer and Amend $SrCO_3$ standard with $Sr^{87}/Sr^{86} = 0.70794$ (NBS, 1973) was run twice during the course of this work, and ratios of 0.7071 ± 0.0008 and 0.7088 ± 0.0012 were obtained. A value of 0.7080 ± 0.0005 is the average of six determinations on this standard in the U. of A. isotope laboratories from 1972 to 1975.

An analysis of Sr in NBS feldspar 607 (NBS 70-a feldspar), a standard reference material, was also carried out and gave the following results:

Sr^{N} = 62.35 p.p.m.
Sr^{87r} = 2.96 p.p.m.
} total Sr = 65.3 p.p.m.

Sr^{87}/Sr^{86} = 1.200

These results compare very favorably with the values (NBS, 1972) stated on the certificate of analysis (total Sr = 65.5 ± 0.3 p.p.m., Sr^{87}/Sr^{86} = = 1.2004 ± 0.0002), or with those of Compston et al. (1969). Two blank determinations using no sample for the total Sr analytical procedure yielded approximately 7 nanogram of Sr^{N} for the blank (as compared to 20 microgram per sample). Analytical precision is thus estimated to include a total error less than 0.5% of the total amount present for Sr analyses.

To calculate Rb concentrations, an atomic ratio of Rb^{85}/Rb^{87} = 2.600 was assumed. Single filament Rb runs usually showed appreciable

isotopic fractionation (1-2%), and the first set of data obtained was selected as closest to the actual value; however, the precision on each set of data was better than two parts per thousand. Three single filament determinations on the same sample of NBS-feldspar 607 yielded results of 516, 509, and 507 p.p.m. for Rb concentration. The NBS certificate of analysis states 524 $\pm$ 1p.p.m., Compston et al. (1969) obtained 530 p.p.m., and deLaeter and Abercrombie (1970) recommend a value of 525 p.p.m. Several unspiked single filament Rb runs on a mixture of Rb and K chloride ("normal" Rb) resulted in values for the Rb^{85}/Rb^{87} ratios from 2.560 to 2.591 as compared to the accepted value of 2.600 (the Shields value is 2.593 $\pm$ 0.002 (Catanzaro et al. (1969))). It can therefore be seen that Rb determinations could be inaccurate by 1-2% due to isotopic fractionation.

Triple filament runs in most cases did not show significant fractionation (over 0.3%); if fractionation was observed, the run was repeated. Thus several sets of data from one run could be averaged. Eight analyses of "normal" Rb yielded Rb^{85}/Rb^{87} = 2.596 $\pm$ 0.005 (one σ). The error is only slightly greater than the standard deviation of data from a single run. Two analyses on the above sample of NBS feldspar indicated 517 p.p.m. Rb; 519,519, and 516 p.p.m. were the results obtained on another sample of the feldspar. These runs again had precision of better than two parts per thousand. Since very small sample weights were used for Rb determinations, another few parts per thousand error may have been introduced in weighing. However, it appears that intralaboratory precision on Rb determinations using triple filaments is better than 0.5%.

2. X-Ray Diffraction

The unheated and some of the heated purified mineral separates were analysed by means of x-ray diffraction. A Philips x-ray instrument was employed and powder photographs were taken using a camera of 57.3 mm. radius with coarse collimators. All minerals except biotite were exposed to Cu Kα radiation with Ni filter for 1.5 hours at 35 kV. and 15 mA. For biotites Fe Kα radiation with Mn filter was utilized at operating conditions of 35 kV., 10 mA., and with 3 hour exposure time. The 2θ positions of the lines were measured, converted to d spacings and compared with tabulations in the ASTM card index. Films were not corrected for shrinkage, since in all cases this appeared to be less than 0.1 mm. Intensity estimates were made visually, with the strongest line assigned an intensity of 100.

3. Microprobe Analysis

Grain mounts of unheated and heated mineral separates were prepared for microprobe study. Mounts in plastic were made of one of the unheated minerals ("B"), and of samples heated for 2.5, 100, 213, 405, 802, and 1079 hours for each of the minerals biotite, muscovite, microcline, and albite. The micas were the same samples previously analysed by mass spectrometry. The feldspars, although slightly contaminated with each other and quartz, could be distinguished under the electron beam. Thin sections of the undisseminated heated and unheated rocks were also prepared for microprobe study.

Total elemental analyses were carried out utilizing an ARL-EMX microprobe with energy dispersive analysis (Smith, ed., 1976). A description of the standards that were selected is given in Table XV.

TABLE XV

Standards Used in Microprobe Analysis

Albite Ab-80: feldspar glass prepared by J.V. Smith

Elemental composition:

Si: 29.63%
Al: 12.20%
Ca: 3.02%
Na: 6.93%
O: 48.22%

Mount number EP/S6-2

Orthoclase Or-1: from Bernard Evans (Berkeley), Ingamells analysed

Elemental composition:

Si: 30.10%
Al: 9.83%
Fe: 0.023% (Fe^{II})
Na: 0.85%
K: 12.39%
O: 46.03%

Mount number EP/S11-3

D-Hypersthene H66: from J.V. Smith

Elemental composition:

Si: 24.70%
Ti: 0.06%
Al: 2.30%
Fe: 11.70% (Fe^{II})
Mg: 16.10%
Mn: 0.20%
Ca: 0.20%
O: 44.44%

Mount number EP/S6-9

Operating conditions included an operating voltage of 15 kV and beam current of 300 nanoamps.

The albite was used as the standard for the elements Al, Ca, and Na; hypersthene for Mg and Fe; and orthoclase for Si and K. Standards for any other elements were not included.

Data were accumulated on magnetic tape for the above standards, for the samples, and for a calibration standard, willemite. Counting times were 400 seconds (corrected for dead time) for each set of data. Using a focussed electron beam, automated beam scanning over an area of approximately 100-400 square microns was utilized in order to obtain a representative average analysis for a grain and to minimize damage to the mineral by the electron beam. The latter effect could be significant in all of the mineral samples and in both feldspar standards. Several grains or parts of grains were analysed within the 400 second counting time for the standards.

On the whole rock thin sections, two to four grains of the mineral to be analysed were located; the sample was moved continuously under the electron beam by hand to reduce the effect of inhomogeneities and to get an average composition for these grains. For the grain mounts of individual minerals, 20 to 25 grains were analysed with beam scanning (near the center of each grain, particularly for the feldspars) during the 400 seconds. The mineral being examined could be recognized by its appearance under reflected light or by the colour of the cathodoluminescent spot produced by electron impact.

It was attempted to analyse all samples of one mineral, e.g. all microclines, sequentially on one day, eliminating effects due to variability of counts on the standards from day to day. The tape data containing

counting statistics on samples and standards were read into the FORTRAN program EDATA, which calculates for output the weight percent concentrations of elements from Na to Zn (plus Zr and Ba). Default values for standards, included in the program, could be used when working standards for some elements were not included in the analysis (Smith, ed., 1976). Thus, for all the trace elements, and one minor element (Ti) in the minerals analysed, default values were utilized as standards. This procedure is quite adequate for the determination of elements present in low concentrations. Accumulated data on the aforementioned standards were used for the determination of the major elements Na, K, Ca, Mg, Fe, Al, and Si.

In the calculation of analytical compositions, minor amounts (less than 0.1% by weight) of trace elements, which could be due to the sample holder, e.g. Zn, or vacuum oil, e.g. S, Cl, were discarded. Some of the output data had to be modified because of incorrect default values in the computer program during part of the time this investigation was being conducted. Further calculations were carried out only on corrected data.

A short APL program CALC was written to convert the analytical data from weight percent elements to weight percent oxides basis using oxide conversion factors (appendix; Smith, ed., 1976). The data were also recalculated to an atomic basis, i.e. the number of ions of each element with respect to a specified number of oxygens. For the albites and microclines, 32 oxygens were assumed. For the muscovites 22 oxygens were selected; this number is approximately equivalent to 24(O, OH) usually quoted in mica analyses, and was more applicable to the heated micas which had lost most of their water contents. Biotite analyses were

calculated assuming all iron to be present in the ferric state, a reasonable assumption for all the heated samples An additional 1 to 1.5 oxygens would be needed to oxidize the Fe^{II} present in the original unheated biotite, therefore, all biotite analyses were calculated on the basis of 23.5 oxygens for the sake of consistency. Very similar ionic concentrations on unheated biotites and muscovites were obtained when H_2O contents and FeO/Fe_2O_3 ratios from Baadsgaard and van Breemen (1970) were used for the calculations on the basis of 24(O, OH), and when numbers of both Fe^{II} and Fe^{III} were computed.

A qualitative investigation of the minerals in grain mounts was also conducted with wavelength dispersive analysis. Three spectrometers were available on the microprobe and were set up to determine Ca, K and Na for the feldspars, and Si, K and Na for the micas. Fifty second counting times were employed to examine 10 to 20 grains of the unheated (or 2.5 hour) and longest heated (1079 hour) minerals. Usually counts were obtained with beam scanning over a small area (approximately 100 square microns) at two locations in each grain. One 50 second count on quartz (containing essentially no Na, K, or Ca and found as a contaminant with albite) was used as an indication of the background count rates for these elements in the feldspars. This procedure was selected to determine the variability of the cation concentrations from grain to grain or within grains.

The presence of concentration gradients within grains was also examined by taking x-ray scanning photographs with the spectrometers set at the wavelengths for various elements of interest. Areas from $(20 \text{ microns})^2$ to $(300 \text{ microns})^2$ were investigated for possible gradients or nucleation

of new phases. Wavelength dispersive counting and beam scanning photographs were done under operating conditions of 15 kV and 100 nanoamps.

B. Microprobe Analyses in Oxide Percents

Analyses of minerals by electron microprobe energy dispersive analysis calculated in terms of oxide percents are given in Tables XVI through XIX. All analyses are of 20 to 25 grains in grain mounts with beam scanning unless otherwise indicated.

Weight percent oxide totals are very high for biotite and albite analyses, possibly due to volatilization of Na and K in the albite glass and orthoclase standards, which would result in too high values for alkalis and too low values for other elements in the samples being analysed. Corrections have been made in the microprobe program, EDATA, since the time that the present analyses were calculated, to account for oil build-up in the microprobe. If the data are recalculated, oxide totals lower by 1% to 2% than the values given in the tables result, well as increased Na (by approximately 0.5% Na_2O) contents and decreases in other elements for the K-containing minerals compared to data in the tables. Thus, volatilization of standards may not have to invoked to account for the high oxide totals. However, since not all the original tape data were available for recalculation, and since the correction appears to be systematic, the original data have been retained. It is believed that the correction would not affect the interpretations of microprobe data in Sections B.1 and B.2 of the Results and Discussion.

Oxide totals for muscovites, on the other hand, are extremely low. A possible explanation is that because of the delamination and expansion of heated muscovite, epoxy was incorporated between sheets of muscovite,

and inadvertently included in areas of analyses, resulting in overall low values for all elements. Also, an improper conducting coating applied to the muscovite mineral mount could result in similar behaviour. When data are recalculated to an atomic basis, the errors in analysis represented by the low oxide totals probably become negligible.

TABLE XVI

Albite Analyses in Weight Percent Oxides

Albite Sample (Heating Time (hours))	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	Σ oxides
O_E*	11.00	21.16	67.54	0.12	1.94	101.77
O_B	11.01	21.09	68.25	0.34	1.63	102.33
2.5	11.03	21.55	68.03	0.32	1.88	102.81
100	11.16	21.62	68.18	0.37	1.82	103.14
213	10.96	21.80	68.11	0.40	2.00	103.27
405	10.89	21.50	67.82	0.49	1.88	102.58
802	10.81	21.77	68.19	0.70	1.96	103.42
1079	10.61	21.69	67.92	0.80	1.94	103.04

* - thin section, average of 4 grains with hand scanning.

O_E and O_B refer to unheated albites E and B.

TABLE XVII

Microcline Analyses in Weight Percent Oxides

Microcline Sample (Heating Time (hours))	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	V_2O_5+BaO**	Σ oxides
O_A*	0.17	18.58	64.33	15.44	---	0.43#	98.93
O_E*	----	18.35	65.75	15.78	---	0.22#	100.09
2.5	0.28	18.73	65.87	16.14	.05	0.66	101.73
100	0.67	18.75	66.06	15.57	---	0.59	101.65
213	0.87	18.81	66.06	15.29	.06	0.85#	101.95
405	1.22	18.78	65.96	14.81	.07	0.57	101.41
802	2.14	18.87	66.56	13.53	.06	0.57	101.72
1079	1.78	18.75	66.19	14.04	.08	0.39	101.24

* - thin section, average of 4 grains with hand scanning

\# - plus ZrO_2, 0.2% approximately

** - approximately equal amounts of V_2O_5 and BaO

TABLE XVIII

Muscovite Analyses in Weight Percent Oxides

Muscovite Sample (Heating Time (hours))	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	TiO_2	Fe_2O_3	V_2O_5	Σ oxides
0_B	0.13	0.25	34.84	46.09	10.72	0.81	1.71	0.21*	94.76
2.5	0.25	0.36	34.68	46.26	10.61	0.68	1.84	0.25**	94.93
100	0.66	0.27	33.83	44.87	9.77	0.86	1.70	0.17	92.12
213	0.73	0.29	34.37	45.11	9.66	0.73	1.82	0.20	92.90
405	0.71	0.21	34.15	44.58	9.65	0.78	1.71	0.17	91.95
802	1.20	0.28	34.78	45.52	9.15	0.82	1.75	0.12	93.62
1079	1.28	0.23	34.49	45.83	9.18	0.92	1.77	0.11	93.81

* - includes 0.08% BaO

** - includes 0.13% BaO

TABLE XIX

Biotite Analyses in Weight Percent Oxides

Biotite Sample (Heating Time (hours))	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	TiO_2	Fe_2O_3	MnO	NiO	ZnO	Σ oxides
$O_{B_2}^1$	----	5.78	18.80	33.42	8.01	2.81	29.33	0.59	0.17	0.16	99.07
O_B^2	----	5.75	18.59	32.77	7.74	2.59	28.82	0.54	----	0.16	96.97
2.5	----	5.43	18.60	34.33	8.83	3.08	28.33	0.57	0.12	0.27	99.55
2.5*	0.12	5.24	18.09	33.84	8.85	3.00	27.37	0.50	0.07	0.10	97.17
100	0.67	5.61	19.20	35.43	7.85	3.19	28.55	0.55	0.19	0.26	101.51
100*	0.56	6.03	19.11	34.72	7.75	3.00	29.56	0.62	0.06	0.13	101.53
213	0.77	5.44	18.94	35.30	7.90	3.17	28.87	0.56	0.22	0.28	101.43
213*	0.82	5.26	18.72	35.22	8.07	3.31	28.08	0.53	----	0.15	100.16
405	1.83	5.67	19.51	36.14	6.52	3.30	29.62	0.62	0.13	0.26	103.60
405*	1.50	6.29	20.04	36.26	6.48	3.00	29.88	0.64	----	0.14	104.23
802	2.39	5.81	19.72	36.69	5.55	3.25	29.90	0.64	0.26	0.42	104.62
802*	2.06	6.19	20.06	36.20	5.13	3.05	29.12	0.60	----	0.29	102.68
1079^1	2.23	5.80	19.59	37.62	5.97	3.36	29.21	0.59	----	0.32	104.89
1079^2	2.20	5.87	19.48	35.25	6.56	3.29	30.88	0.52	0.07	0.25	103.34

* - analysis with static probe on 20 to 25 grains of grain mounts; other analyses refer to beam scanning on 20 to 25 grains of grain mounts.

	MgO	Al_2O_3	SiO_2	K_2O	TiO_2	Fe_2O_3#	FeO#	MnO	NiO	ZnO	H_2O#	Σ oxides
$O_{B_2}^1$	5.78	18.80	33.42	8.01	2.81	5.87	21.12	0.59	0.17	0.16	4.60	101.31
O_B^2	5.75	18.59	32.77	7.74	2.59	5.77	20.75	0.54	----	0.16	4.60	99.26

- H_2O and Fe_2O_3/FeO ratios from Baadsgaard and van Breemen (1970)
1 & 2 superscripts refer to duplicate analysis done on the same sample.